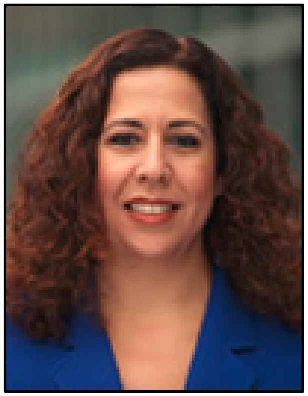
# Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches at Chlorinated Solvent Sites

March 19, 2015

# Welcome and Introductions

Rula Deeb, Ph.D.
Webinar Coordinator



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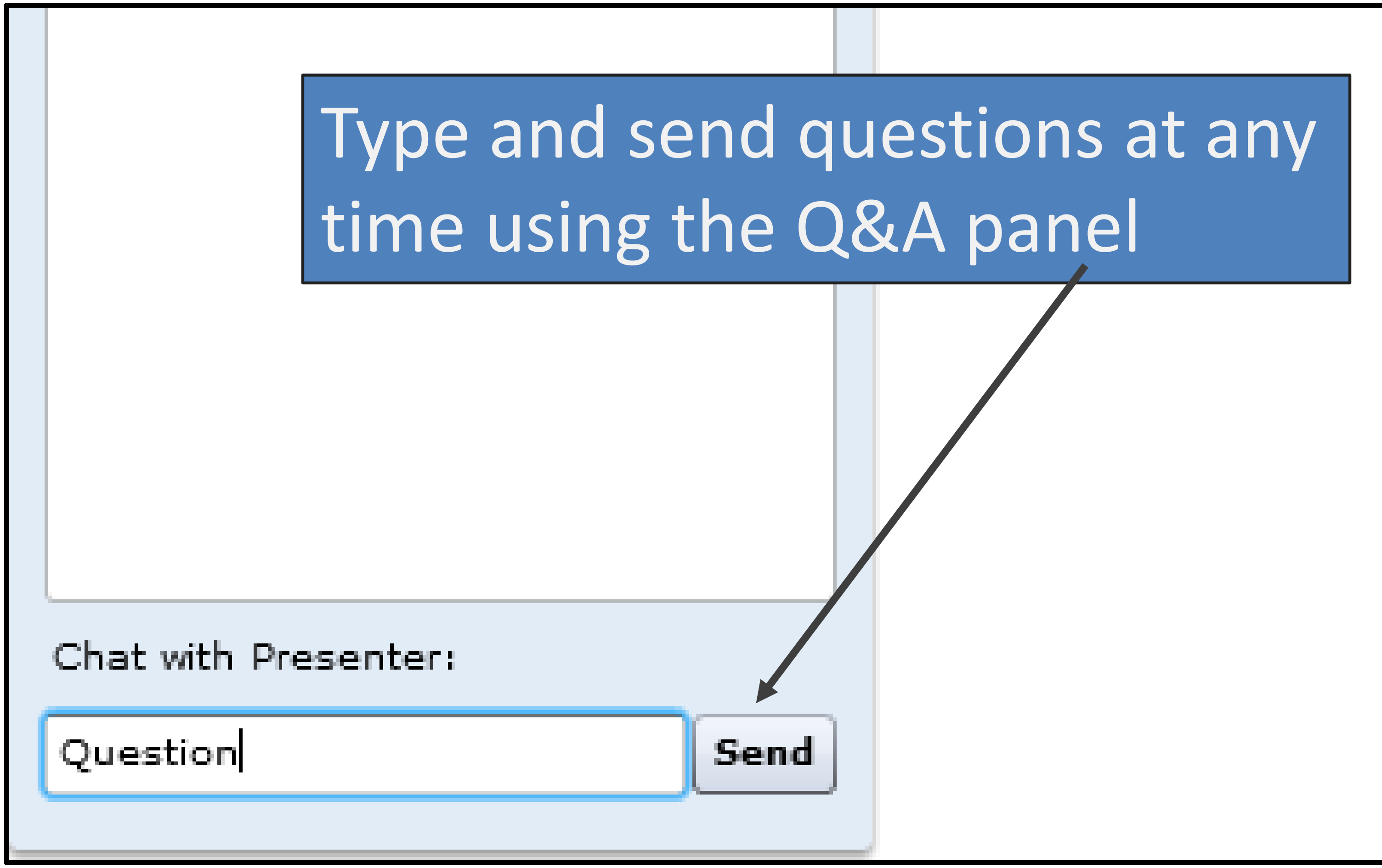
# Webinar Agenda

- Webinar Overview and ReadyTalk Instructions
  Dr. Rula Deeb, Geosyntec (5 minutes)
- Overview of SERDP and ESTCP
  Dr. Andrea Leeson, SERDP and ESTCP (5 minutes)
- Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches at Chlorinated Solvent Sites
  Ms. Carmen Lebrón, Independent Consultant (20 minutes + Q&A)
  Dr. John Wilson, Scissortail Environmental (40 minutes + Q&A)
- Final Q&A session

# How to Ask Questions



# SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
Environmental Restoration
Program Manager

SERDP
DOD • EPA • DOE

ESTCP

# SERDP

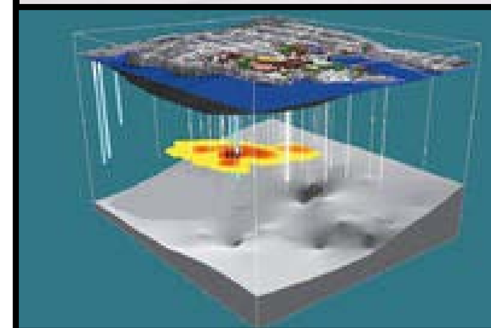
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

# ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

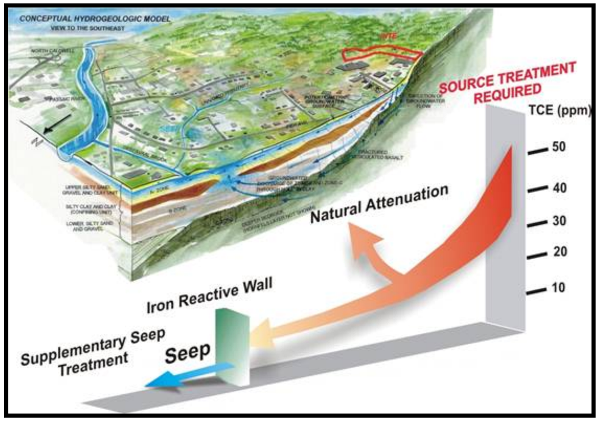
# Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Climate Change
5. Weapons Systems and Platforms



# Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment




# SERDP and ESTCP Webinar Series

| DATE | WEBINARS AND PRESENTERS |
|---|---|
| March 26, 2015 | **Innovative Tools for Species Inventory, Monitoring, and Management**<br>• Dr. Caren Goldberg, Washington State University<br>• Dr. Lisette Waits, University of Idaho |
| April 16, 2015 | **Blast Noise Measurements and Community Response**<br>• Mr. Jeffrey Allanach (Applied Physical Sciences Corp.)<br>• Dr. Edward Nykaza (U.S. Army Engineer Research and Development Center) |
| May 7, 2015 | **Munitions Mobility** |
| May 28, 2015 | **Managing Munition Constituents on Training Ranges**<br>• Dr. Paul Hatzinger (CB&I Federal Services)<br>• Dr. Thomas Jenkins (Thomas Jenkins Environmental Consulting) |

# Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches at Chlorinated Solvent Sites

**ESTCP Project ER-201129**

Carmen Lebrón, Independent Consultant
Dr. John T. Wilson, Scissortail Environmental Solutions, LLC

# Project Objectives and Technical Approach

Carmen Lebrón
Independent Consultant

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# Presentation Outline

- Background
  - Project objectives and goals
  - Technical approach (Tasks)
- Framework application
  - Review of regulator requirements
  - Intended application of the framework
  - Decision logic in a decision support tool
  - Case studies
    - Extracting rate constants for degradation
    - Dhc density to explain the rate of degradation
    - Magnetic susceptibility to explain the rate of degradation

# Other Team Members

- Todd Wiedemeier, Wiedemeier and Associates
- Dr. Frank Löffler, University of Tennessee
- Yi Yang, University of Tennessee
- Mike Singletary, NAVFAC SE
- Dr. Rob Hinchee, Integrated Science and Technology, Inc.





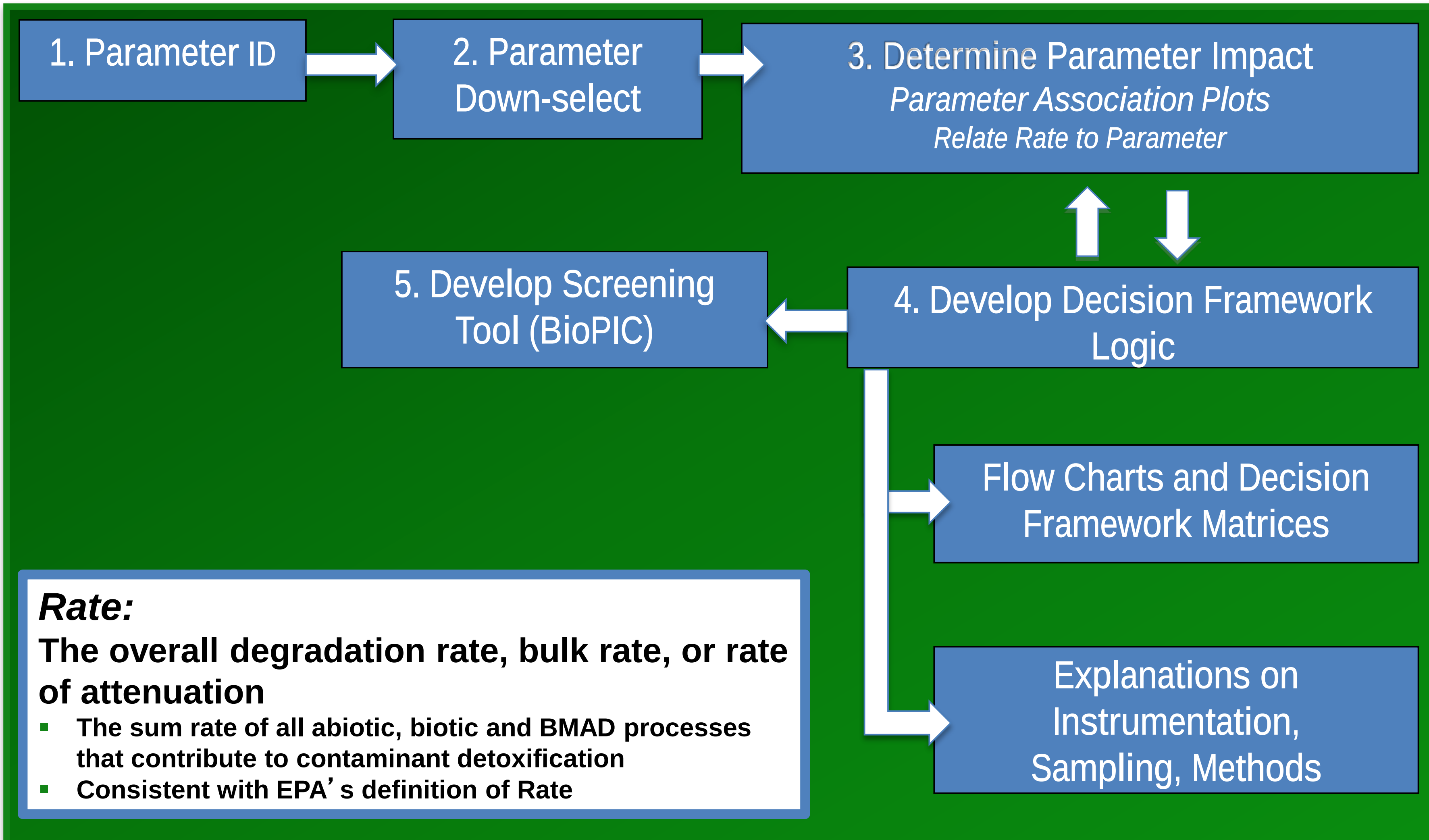
# Technical Goals

- Incorporate new science (tools, methods and findings) into a decision making framework addressing EPA's OSWER Directive 9200.4-17P
  - Monitored Natural Attenuation (MNA)
- Integrate the decision-making framework into an easy to use application
  - Excel spreadsheet
- Guide users in the selection of MNA, biostimulation and bioaugmentation

**EPA/600/R-98/128**
**September 1998**

Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

# Technical Approach




***Rate:***

**The overall degradation rate, bulk rate, or rate of attenuation**

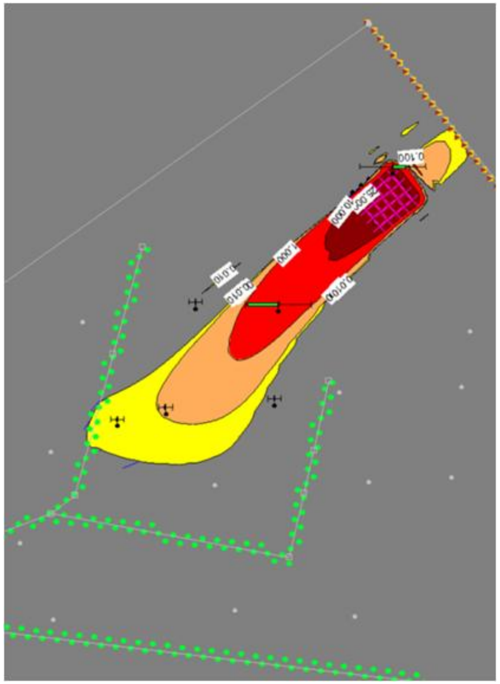
- **The sum rate of all abiotic, biotic and BMAD processes that contribute to contaminant detoxification**
- **Consistent with EPA's definition of Rate**

# Pathways Addressed in Framework

Groundwater sample

Soil Sample

| Degradation Pathways |
|---|
| **Complete Anaerobic Reductive Dechlorination (RD)**<br>*(groundwater parameter)* |
| **Partial Reductive Dechlorination**<br>*(groundwater parameter)* |
| **Aerobic Biological Oxidation**<br>*(groundwater parameter)* |
| **Abiotic Degradation**<br>*(soil parameter)* |



***EPA 1998 Protocol dealt only with reductive dechlorination***

# Task 1. Parameters' Identification

- Began with the EPA 1998 parameters
- Classified parameters based on:
  - Parameter important in determining a degradation pathway
  - Confidence in the analytical results

| *Parameters from EPA, '98 Protocol* | | | |
|---|---|---|---|
| Oxygen | pH | VFAs | DCA |
| Nitrate | TOC | BTEX | Carbon Tet |
| Iron II | Temperature | PCE | Chloroethane |
| Sulfate | Carbon Dioxide | TCE | Ethene/Ethane |
| Sulfide | Alkalinity | DCE (all 3) | Chloroform |
| Methane | Chloride | VC | Dichloromethane |
| ORP | Hydrogen | 1,1,1-TCA | |

# Parameters Specific to Pathways

| *Parameters of Interest* | *Pathway Applicable To* |
|---|---|
| **Concentrations of PCE, TCE, DCEs and VC** | **All Pathways** |
| **Dissolved Oxygen (DO)** | **All Pathways** |
| **pH** | **All Pathways** |
| **Fe(II)** | **RD, Partial RD, Abiotic** |
| **$H_2S/HS^-$** | **RD, Partial RD, Abiotic** |
| **Ethene** | **All Pathways** |
| ***Dhc* density (Ratio of *Dhc* to Total Bacteria)** | **RD, Partial RD** |
| **Ratio of *bvcA* and *vcrA* to *Dhc*** | **RD, Partial RD** |
| **Bioavailable Organic Carbon (BOC)** | **RD, Partial RD** |
| **Magnetic Susceptibility** | **Abiotic** |
| **Acid Volatile Sulfide** | **Abiotic** |

# Task 2: Down-Select Parameters

| *Parameters of interest* |
|---|
| Concentrations of PCE, TCE, DCEs and VC |
| Dissolved Oxygen (DO) |
| pH |
| Fe(II) |
| $H_2S/HS^-$ |
| Ethene |
| Ratio of *Dhc* to Total Bacteria (Dhc density) |
| Ratio of *bvcA* + *vcrA* to *Dhc* |
| Bioavailable Organic Carbon (BOC) |
| Magnetic Susceptibility (abiotic only) |
| Acid Volatile Sulfide (abiotic only) |

From EPA, 1998 (green rows) — New Parameters (white rows)

***Focus on parameters which:***

- We could relate to impact on rate
- We have confidence in the analytical results
- Data in sufficient statistical amount was available

# Task 3: Estimate Parameter Impact on Rate

- Performance objective: To establish association (impact) using at least 10 data points (wells/transects/sites) for each parameter
  - How do different values for each parameter affect the rate constant?
- Well-known published sites were used as Poster-Child sites

| Destruction Pathway | Poster Child Site |
|---|---|
| Complete Anaerobic Reductive Dechlorination | NAS North Island, Site 5 |
| Partial Reductive Dechlorination | Kings Bay<br>NAS Whiting Field |
| Aerobic Biological Oxidation | Little Creek<br>Tooele Army Depot, UT<br>Hill OU2 |
| Abiotic Degradtion | Twin Cities AAP (*Ferrey & Wilson*)<br>Hopewell Superfund Site (*Wilson*)<br>Massachusetts Military Reservation<br>Former AFB Plattsburgh<br>Oscoda |

| |
|---|
| BIOCHLOR Database / C. Newell<br>*93 sites* |
| ER0518 Database / E. Petrovskis<br>*4 sites* |
| ER2131 database /R. Borden<br>*40 ERD sites, >800 wells* |
| Moffett Field / SWFEC and CB&I<br>*1 site 26 locations* |
| Microbial Insights (MI) data used to correlate qPCR data for *Dhc* abundances with VOC concentration and other biogeochemical datasets with rates |

# Task 3: Estimate Parameter Impact on Rate

WATERRESEARCH40(2006)3131–3140

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ScienceDirect

journal homepage: www.elsevier.com/locate/watres

IWA WATER RESEARCH

## Relationship between *Dehalococcoides* DNA in ground water and rates of reductive dechlorination at field scale

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a r t i c l e i n f o

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Available online 4 August 2006

*Keywords:*
Ground water Chlorinated ethylenes
*Dehalococcoides* DNA Rate constants
Reductive dechlorination Natural attenuation

Certain strains of *Dehalococcoides* bacteria can dechlorinate chlorinated ethylenes to harmless products. This study was conducted to determ ... ntitative real time polymerase chain reaction (q-PCR) with DNA primer set specific for *Dehalococcoides* organisms. Dechlorination rate constants were extracted from field data using the BIOCHLOR software. Of the six conventional plumes surveyed, ''generally useful'' rates of dechlorination (greater than or equal to 0.3 per year) of *cis*-dichloroethylene (*cis*-DCE) and vinyl chloride (VC) along the flow path were observed at three sites where *Dehalococcoides* DNA was detected, and little attenuation of *cis*-DCE and VC occurred at two sites where *Dehalococcoides* DNA was not detected. At the two sites where there was no net direction of ground water flow, the relationship between the density of *Dehalococcoides* DNA in ground water and the trend in concentrations of chlorinated ethylenes over time in monitoring wells was not so consistent as that observed for the conventional plumes. A comparison of our study to a field study performed by Lendvay and his coworker indicated that monitoring wells did not efficiently sample the *Dehalococcoides* organisms in the aquifer.



*WATER RESEARCH 40 (2006) 3131 – 3140*

- Purpose of the study was to determine if there was a valid correlation between Dhc density and observed reductive dechlorination rate at 6 sites
- Spearman correlation used to analyze relationship between Dhc densities and reductive dechlorination rates
- Useful rates (> 0.3 per year) of cis- DCE and VC observed where Dhc was present
  - Very little degradation observed where Dhc was not detected
- An argument can be made for MNA if Dhc >10E7

# Lu, Wilson and Kampbell, 2006

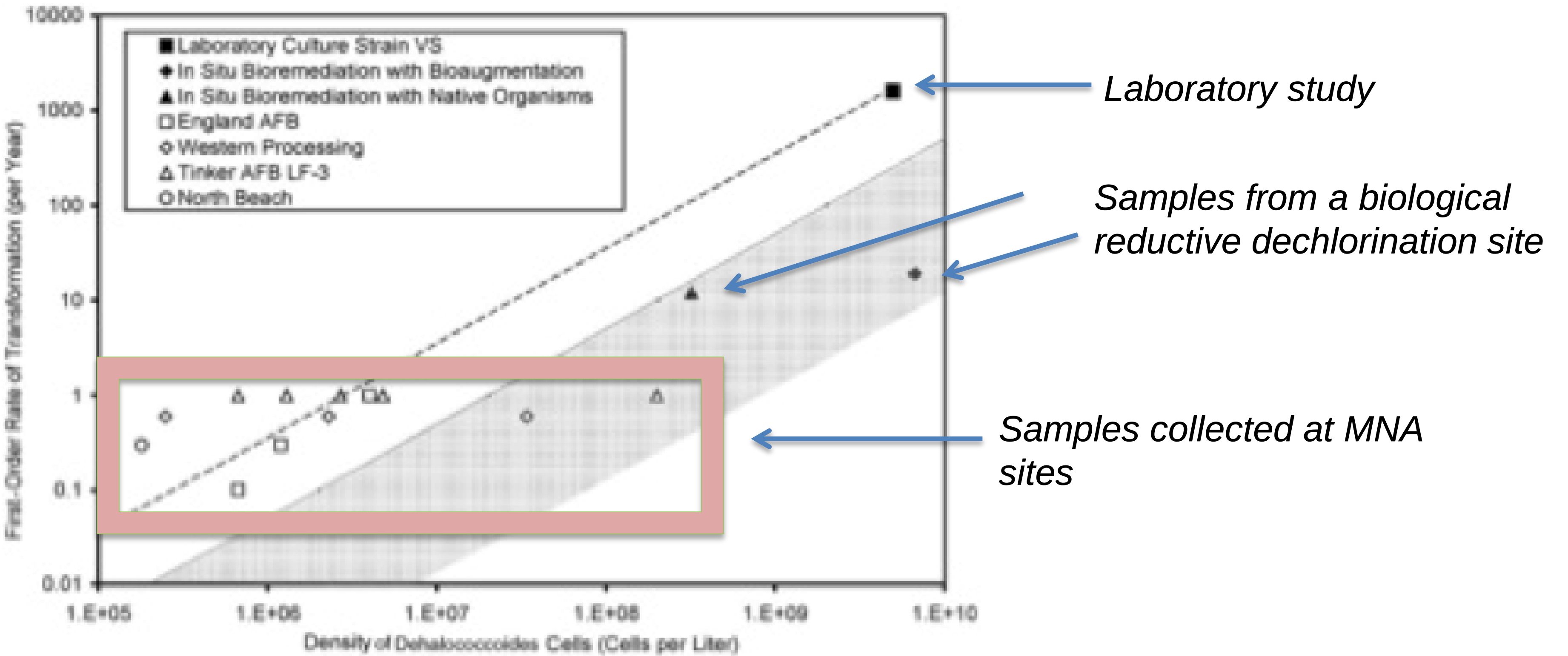
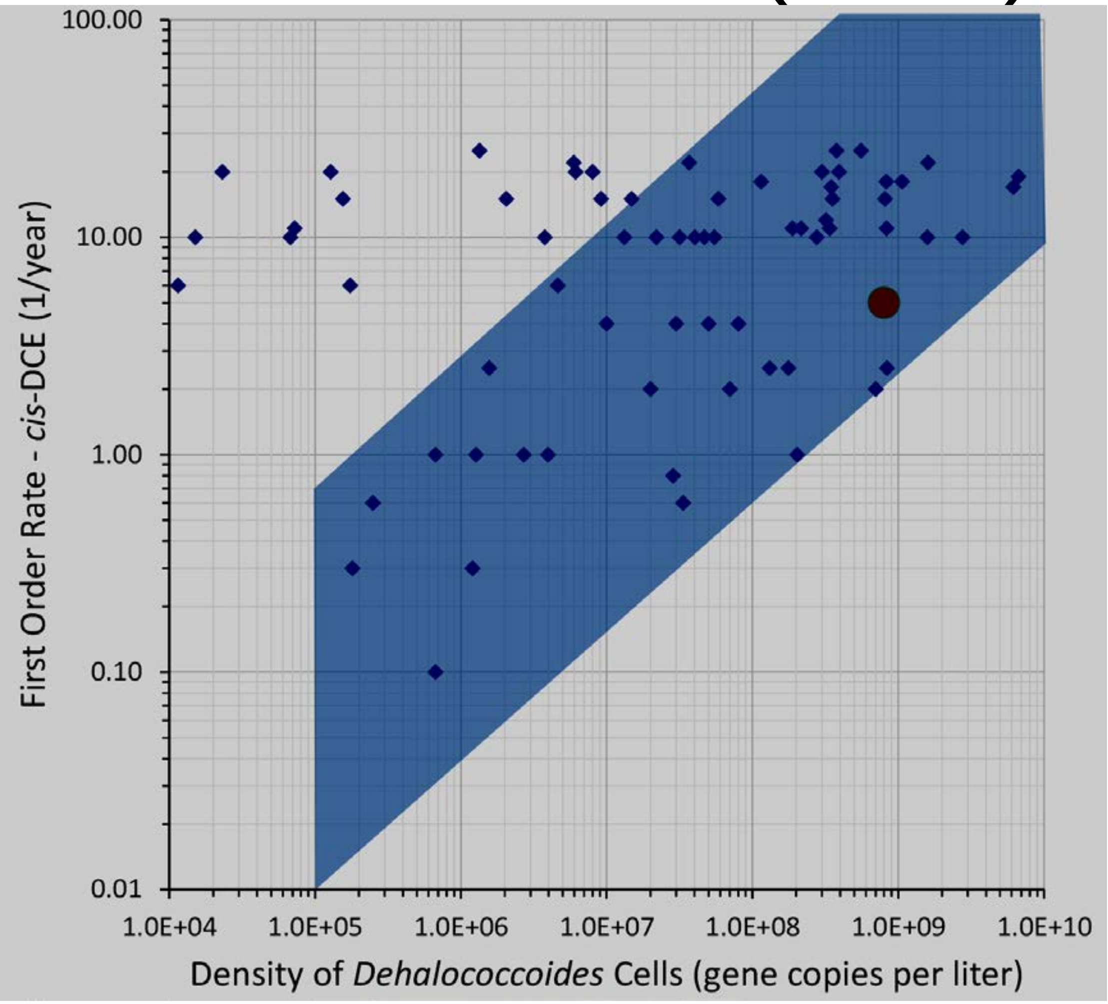



*Fig. 2 – Relationship between the **density of Dehalococcoides cells**) and **the first-order rate of attenuation of cis-DCE in ground water**. The data points with **an open symbol** are from ground water **samples collected at natural attenuation sites**. The data points with a solid diamond symbol or a solid triangle symbol are from sediment samples from a site where biological reductive dechlorination was used to clean up a PCE spill (Lendvay et al., 2003). The data point with a solid square symbol is from a laboratory study of cis-DCE transformation by Dhc strain VS growing under optimum conditions (Cupples et al., 2004).*

# Distribution Plot: *cis*-DCE vs. Dhc (2015)




- Example: Can the attenuation rate be explained by Dhc?
- In which cases can the rate constant be attributed to the cell densities?
  - Draw line from 1.0E+05 to 1.0E+10
  - Draw another line (same slope) encompassing attained rates
  - Upper boundary explains the rate

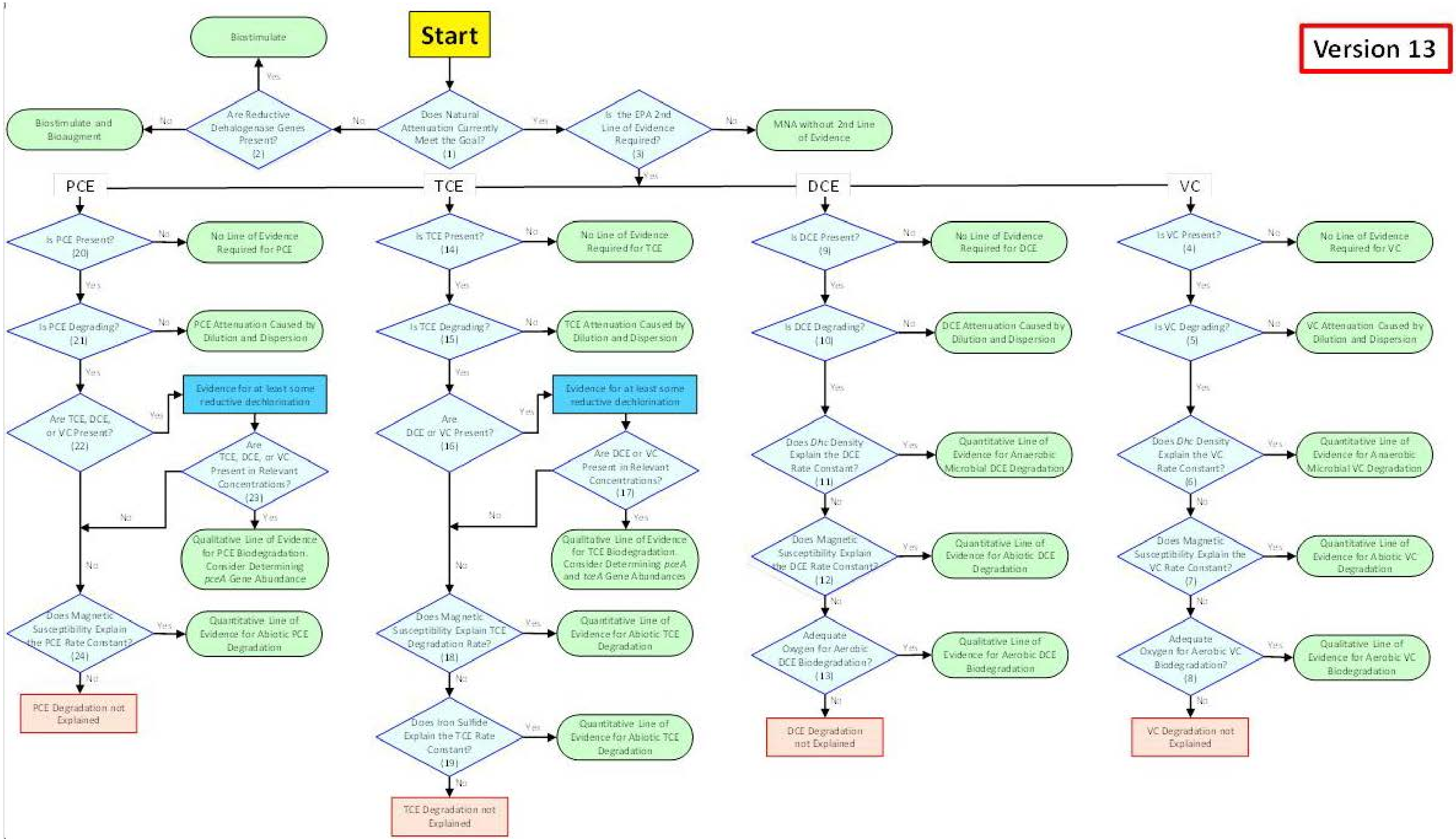
# Related rates of PCE, TCE, *cis*-DCE and VC attenuation to these parameters:

- Dhc
- Dhc/Total Bacteria
- Rdases
- Rdases/Dhc
- DO
- ORP
- Magnetic susceptibility
- Fe(II)
- Mn(II)
- $CH_4$
- Ethene
- TOC (in $H_2O$)
- VC concentration
- Rdases vs. VC concentration

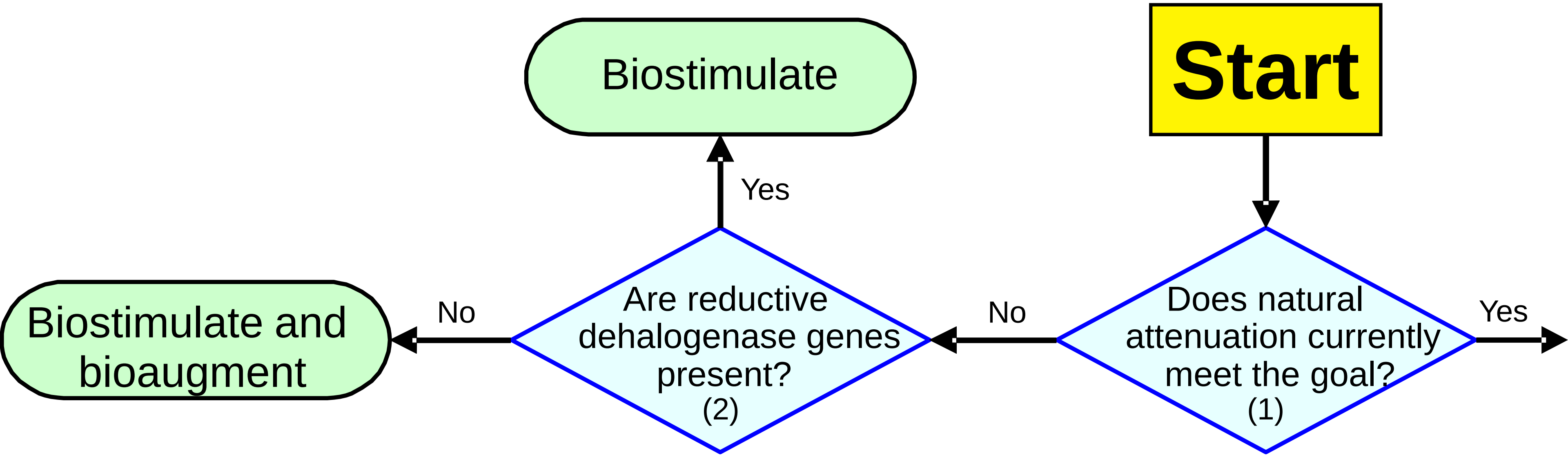
# Task 4: Framework Development

- Parameters found to have a direct correlation on attenuation rate:
  - Dhc density (for TCE, cDCE, and VC only)
  - Magnetic susceptibility
  - FeS
  - $CH_4$
  - Fe(II)
- Used these parameters to develop decision framework logic

# Task 4: Framework Logic



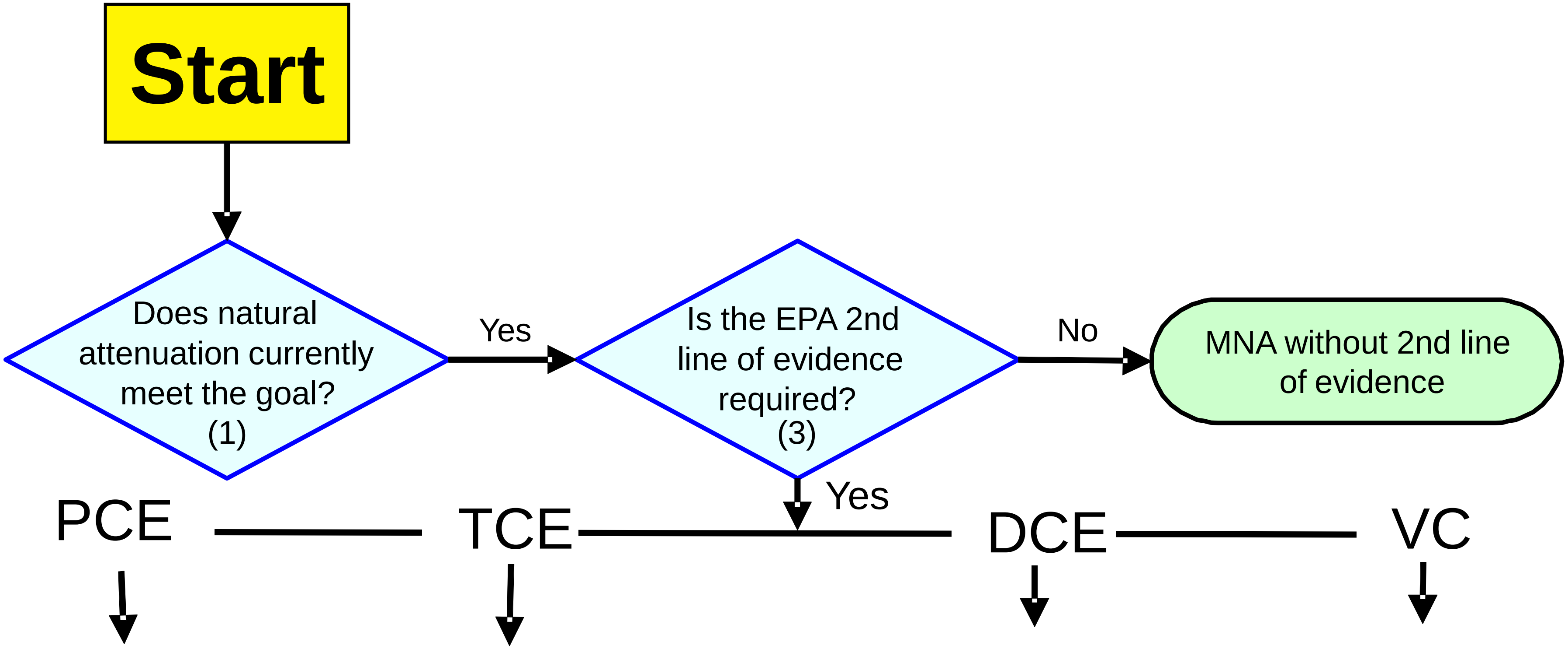
# Task 4: Framework Logic



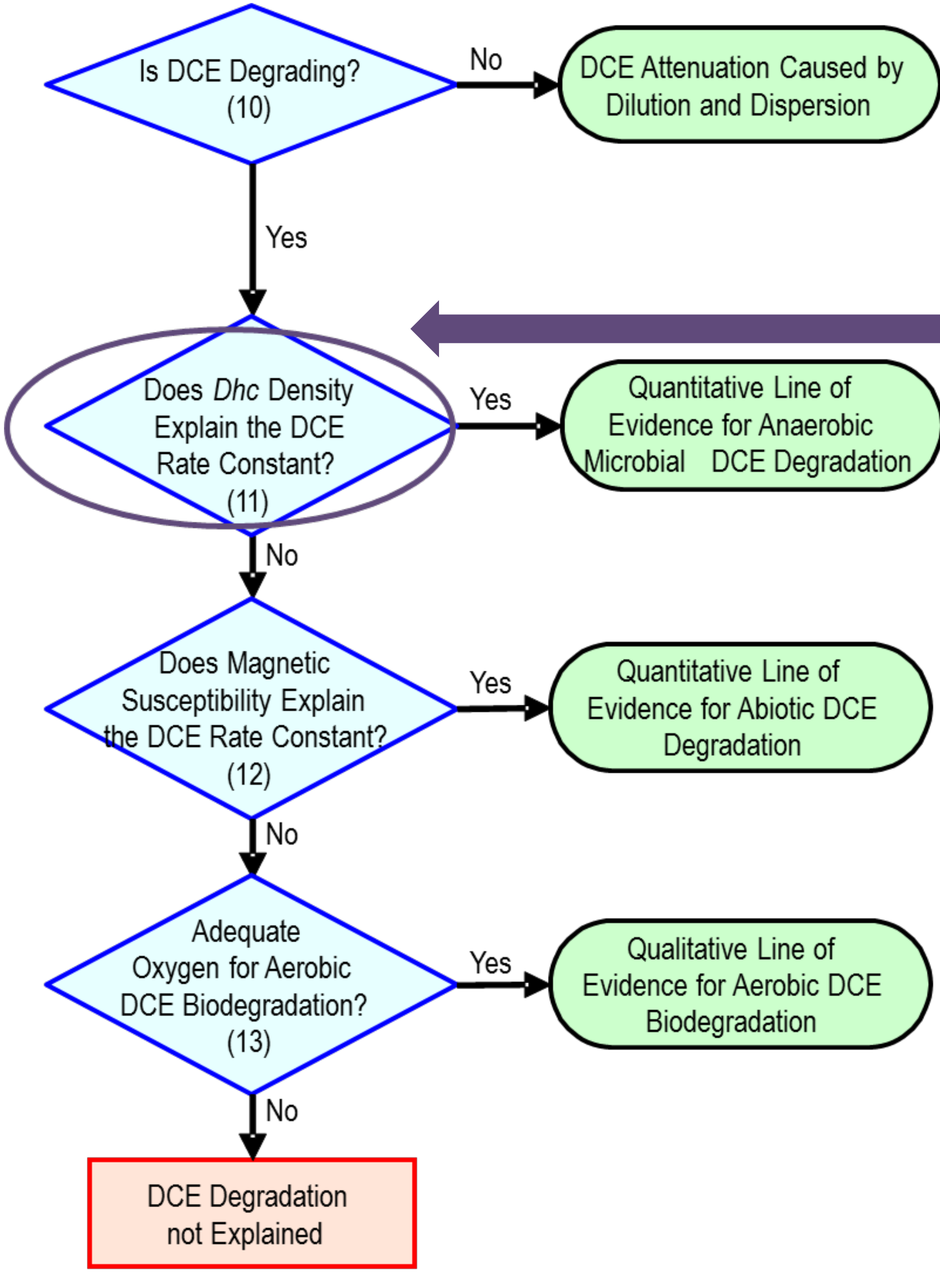

**Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites**

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Directive 9200.4-17P

# Task 4: Framework Logic



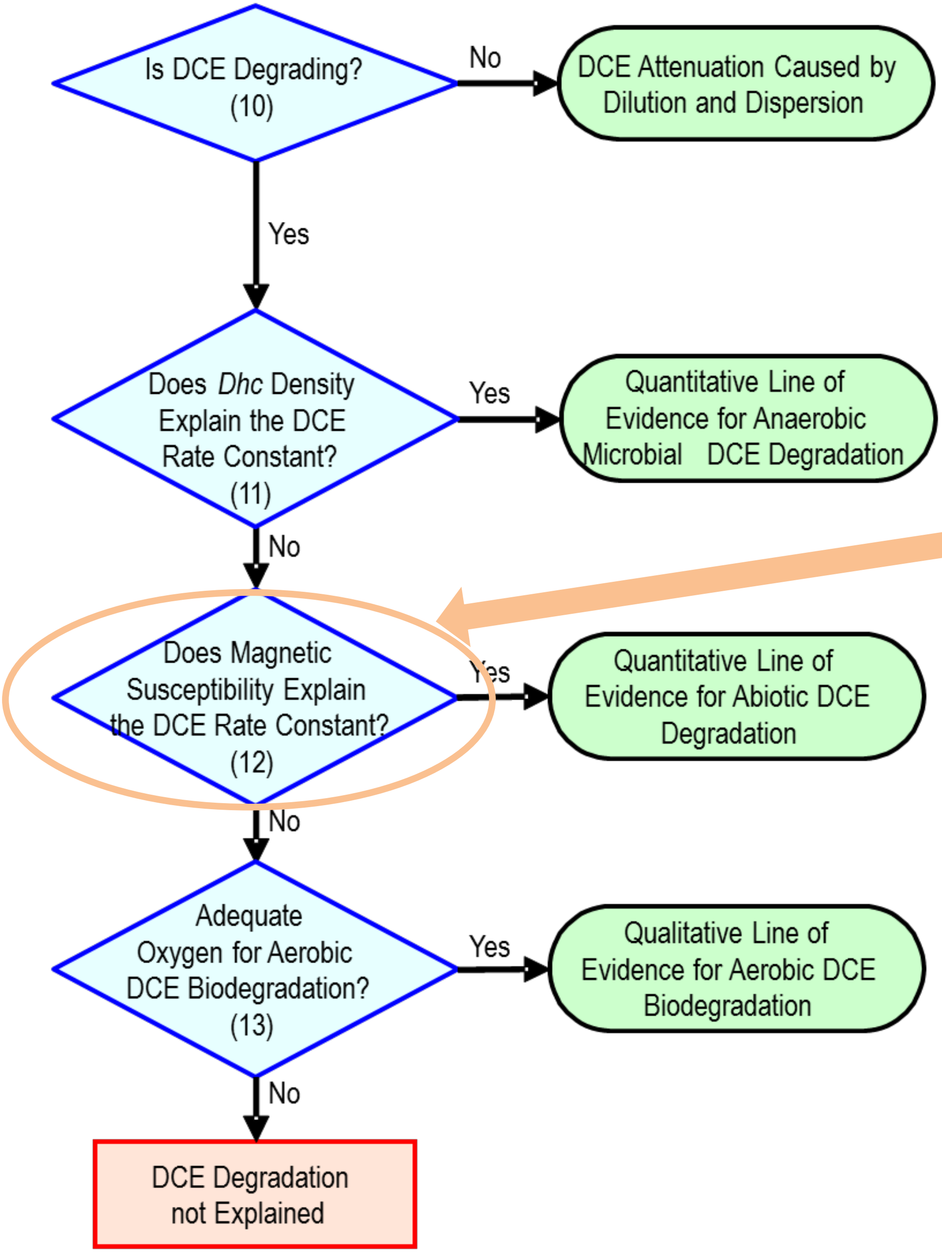
# Framework Logic




Compare the rate of degradation and the density of Dehalococcoides bacteria at the site to the rate of degradation and the density of Dehalococcoides at benchmark sites

Use the spreadsheet Dhc explains rates.xlsx

# Framework Logic



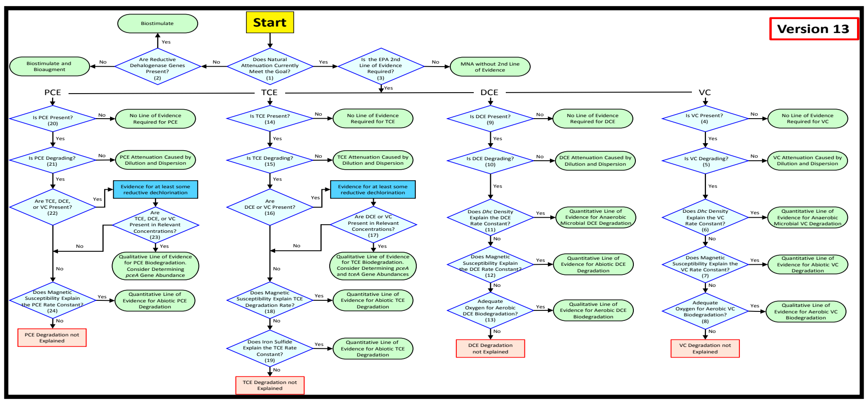

Compare the magnetic susceptibility and rate of abiotic degradation at the site to the magnetic susceptibility and rate of abiotic degradation of *cis*-DCE at benchmark sites

Use the spreadsheet *Magnetic Susceptibility explains rates.xlsx*

# Task 5: Bio Pathway Identification Criteria (BioPIC )

**BioPIC: Pathway Identification Criteria**

A Decision Guide to Achieve Efficient Remediation of Chlorinated Ethenes



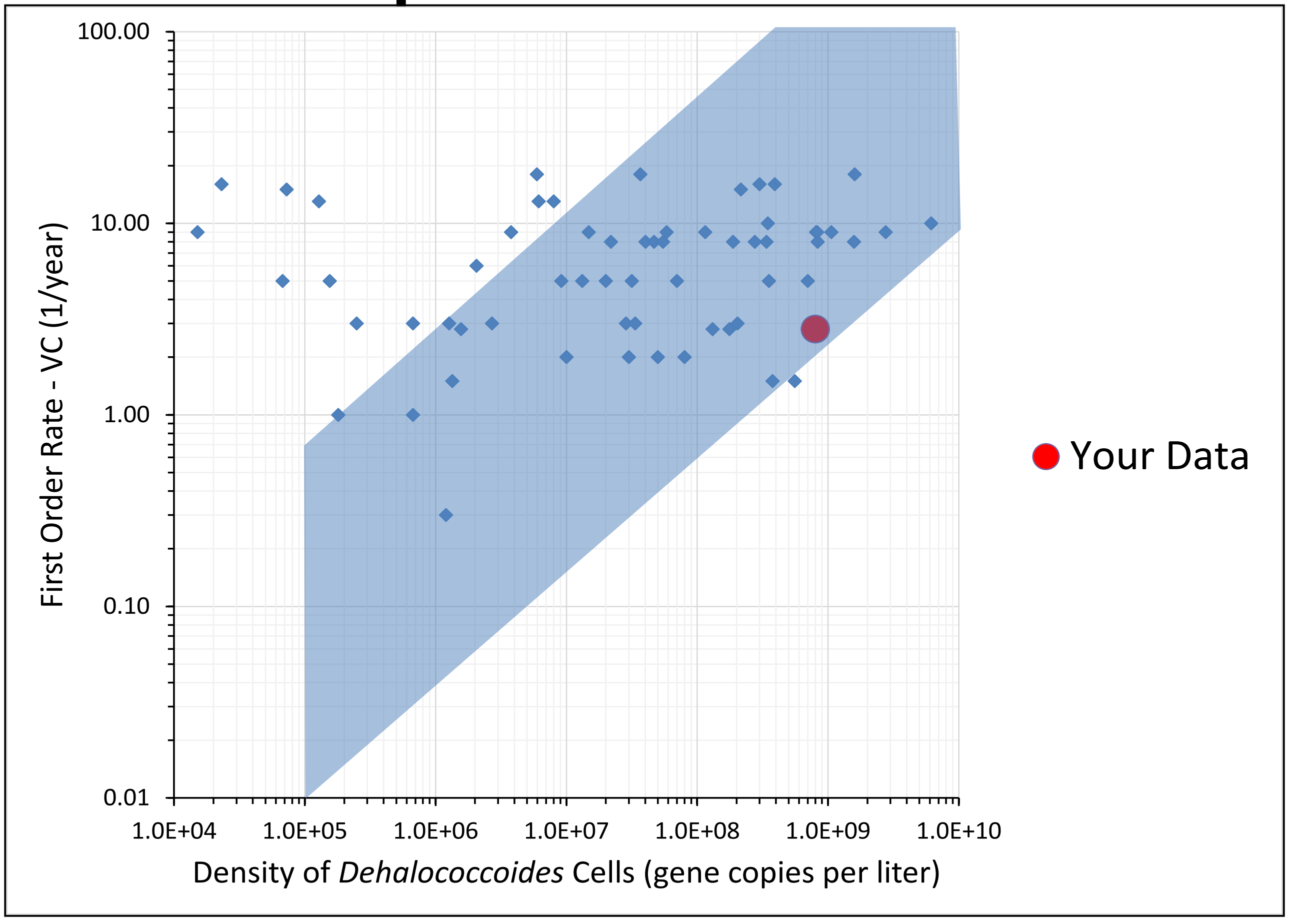

| | | | | | |
|---|---|---|---|---|---|
| 1 | Does Natural Attenuation Meet the goal? | YES | NO | Decision Criteria | Help |
| 3 | Is the EPA 2nd Line of Evidence Required? | YES | NO | Decision Criteria | Help |
| | | PCE | TCE | DCE | VC |
| 4 | Is VC present? | YES | NO | Decision Criteria | Help |
| 5 | Is VC degrading? | YES | NO | Decision Criteria | Help |

Can biotic degradation by *Dehalococcoides* bacteria explain the field scale rate constant for degradation?

| | | | | | |
|---|---|---|---|---|---|
| | Overwrite Input Cells with Data Specific to Your Site | | | | |
| | Input | | | | |
| | First order rate constant for degradation per year | | | pCR Assay Gene Copies per Liter | |
| TCE | | | *Dehaloccoides* 16sRNA | 8.00E+08 | |
| cis-DCE | 2.5 | | | | |
| Vinyl Chloride | 2.8 | | | | |

Excel Spreadsheet ***Dhc explains rates.xlsx***

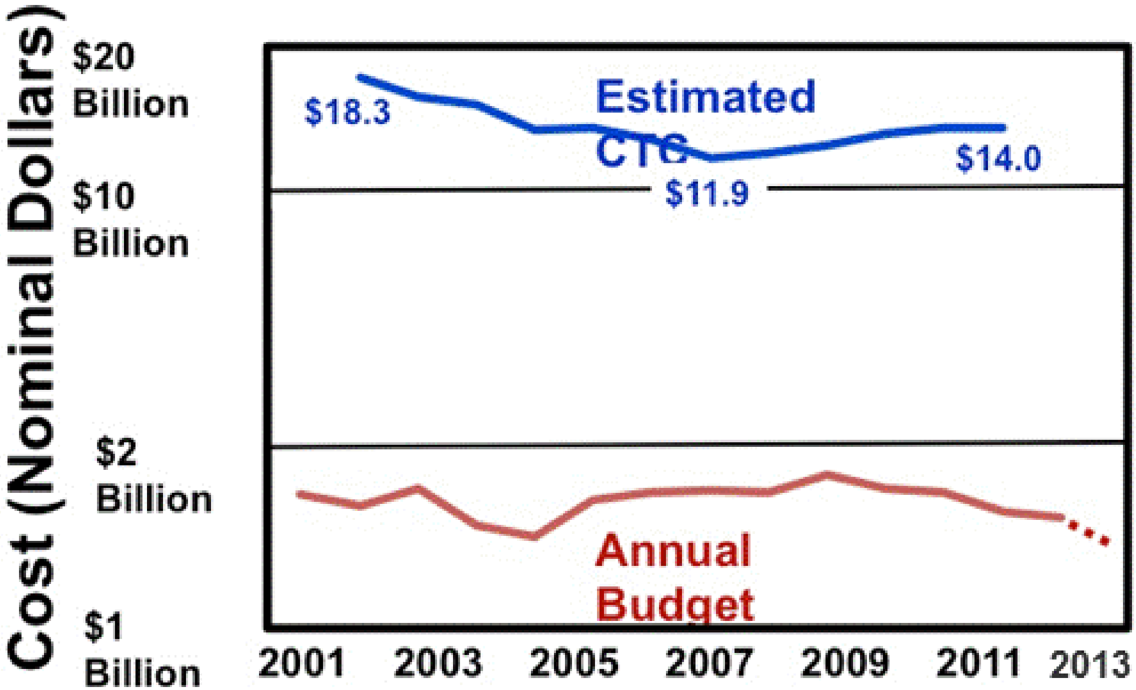
# Impact to Users




**If your data falls within the blue shape defined by the benchmark Poster Child sites, then the density of Dhc can explain your rate constant**

# Benefits to DoD

- Framework enables more focused site characterization tailored to the predominant detoxification pathways
- Follows EPA's MNA guidance
- Guides users in the most appropriate bioremediation approach




Defense Environmental Restoration Program Annual Reports to Congress http://www.denix.osd.mil/arc/

# Q&A Session 1

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# Project Results and Conclusions

Dr. John T. Wilson
Scissortail Environmental Solutions, LLC

SERDP DOD · EPA · DOE | ESTCP

# USEPA Primary Guidance Document for MNA

Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites

U.S. Environmental Protection Agency Office of Solid Waste and Emergency Response Directive 9200.4-17P

# USEPA Primary Guidance Document for MNA (Cont'd)

- *"Once site characterization data have been collected and a conceptual model developed, the next step is to evaluate the potential efficacy of MNA as a remedial alternative"*
- *"This involves collection of site-specific data sufficient to estimate with an acceptable level of confidence both the **<u>rate of attenuation processes</u>** and the **<u>anticipated time required</u>** to achieve remediation objectives"*

# USEPA Primary Guidance Document for MNA (Cont'd)

***A Tiered Approach***

1. …Historical groundwater … data that demonstrate a clear and meaningful trend of decreasing contaminant … concentration over time at appropriate monitoring or sampling points
2. Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the **rate** at which such processes will reduce contaminant concentrations to required levels

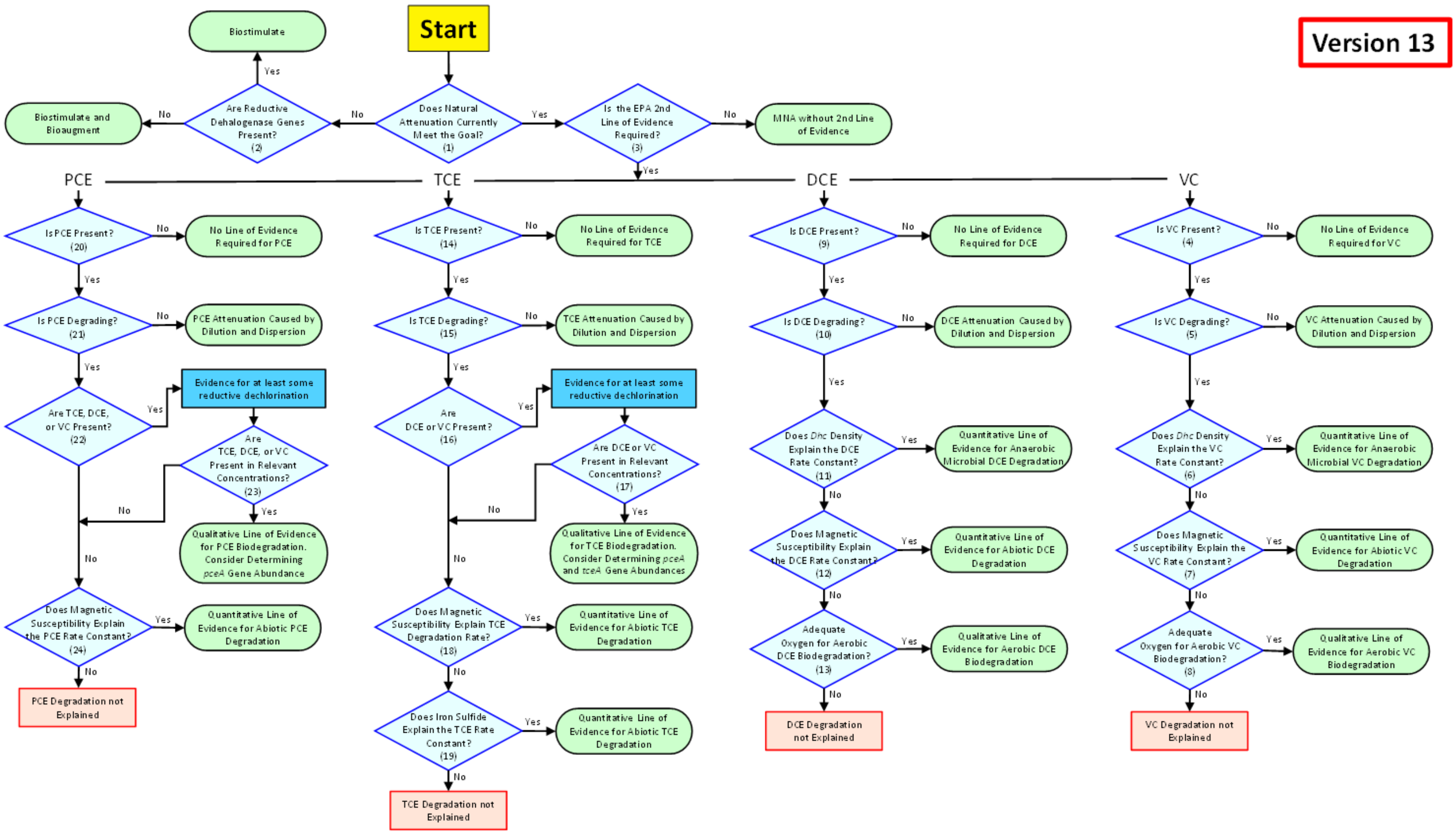
# Proposed Framework

- The framework is intended to answer the following question: “Will a plume impact a receptor?”
  - Will the rate of attenuation bring the highest concentrations in groundwater to acceptable concentrations before the groundwater reaches the receptor of the sentry well?
  - Evaluated by extracting a rate constant from field data for the rate of degradation necessary to meet the goal

# The Framework and BioPIC are not useful to answer this question

- Is the entire plume required to meet the goal?
  - The performance depends on the success of source treatment and the kinetics of natural attenuation of the source
  - These processes can not be evaluated or understood based on the rate of degradation of contaminants in groundwater

# Decision Logic



# BioPIC Example

| | | | | | |
|---|---|---|---|---|---|
| 1 | Does Natural Attenuation Meet the goal? | YES | NO | Decision Criteria | Help |
| 3 | Is the EPA 2nd Line of Evidence Required? | YES | NO | Decision Criteria | Help |
| | | PCE | TCE | DCE | VC |
| 4 | Is VC present? | YES | NO | Decision Criteria | Help |
| 5 | Is VC degrading? | YES | NO | Decision Criteria | Help |

# <u>CASE STUDY</u>
# EXTRACTING THE RATE CONSTANTS

Installation Restoration Site 5-Unit 2 (Golf Course Disposal Area)
North Island Naval Air Station, San Diego, California


LOMA
Cabrillo Memorial Dr


Figure 6.2
Aerial Photograph Showing
Approximate Extent of Unit 2
IR Site 5 - Unit 2
Naval Air Station North Island
San Diego, California

NFECSW

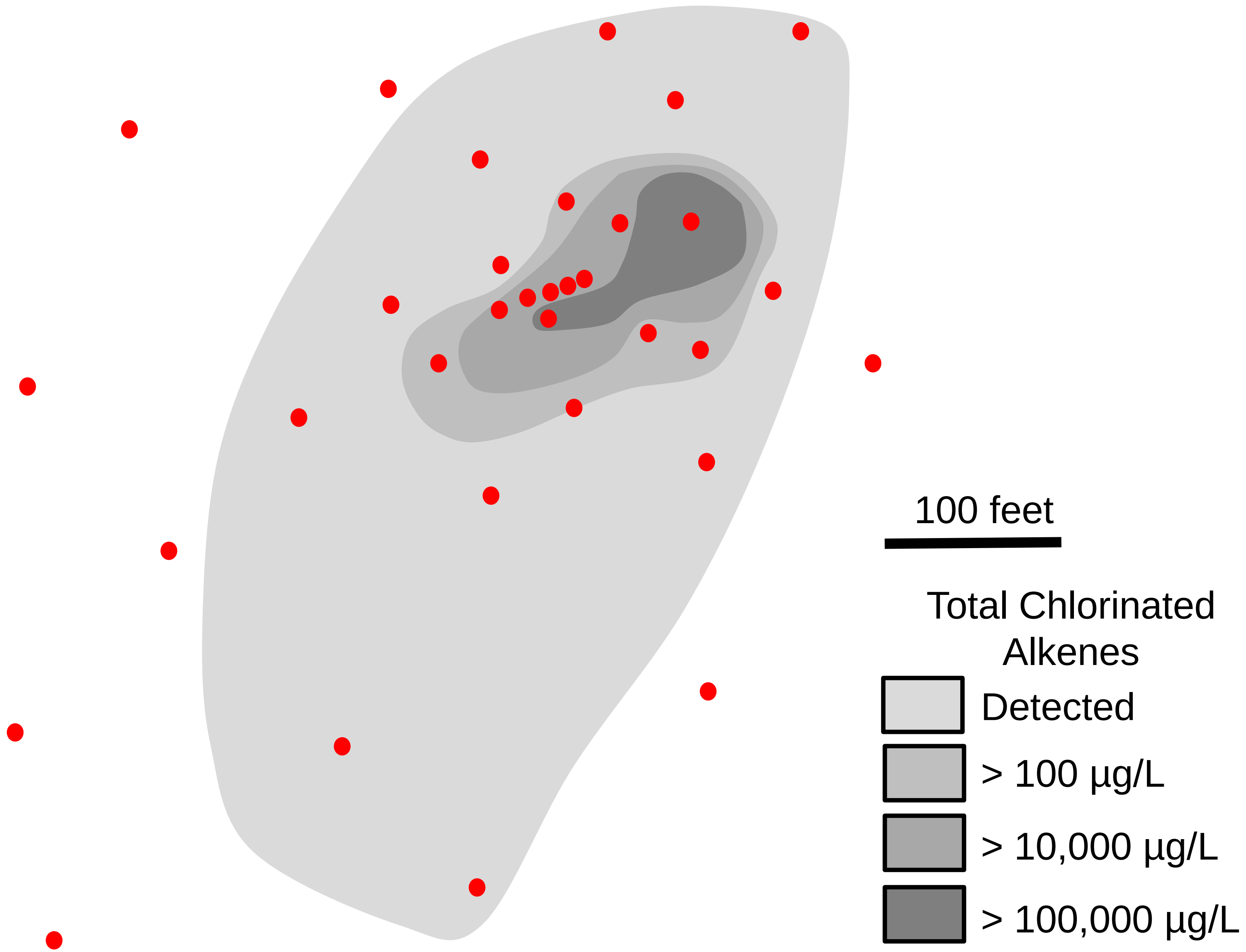
WIEDEMEIER & ASSOCIATES

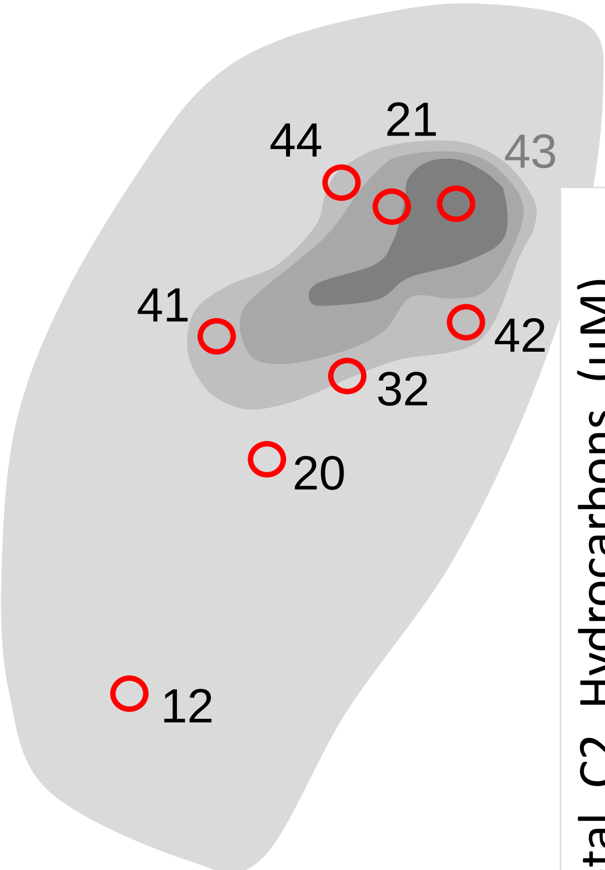
Date: 2/2/10
Client: United States Navy
Project Number: 09001
Revision Number: 0

# Regulatory Boundary

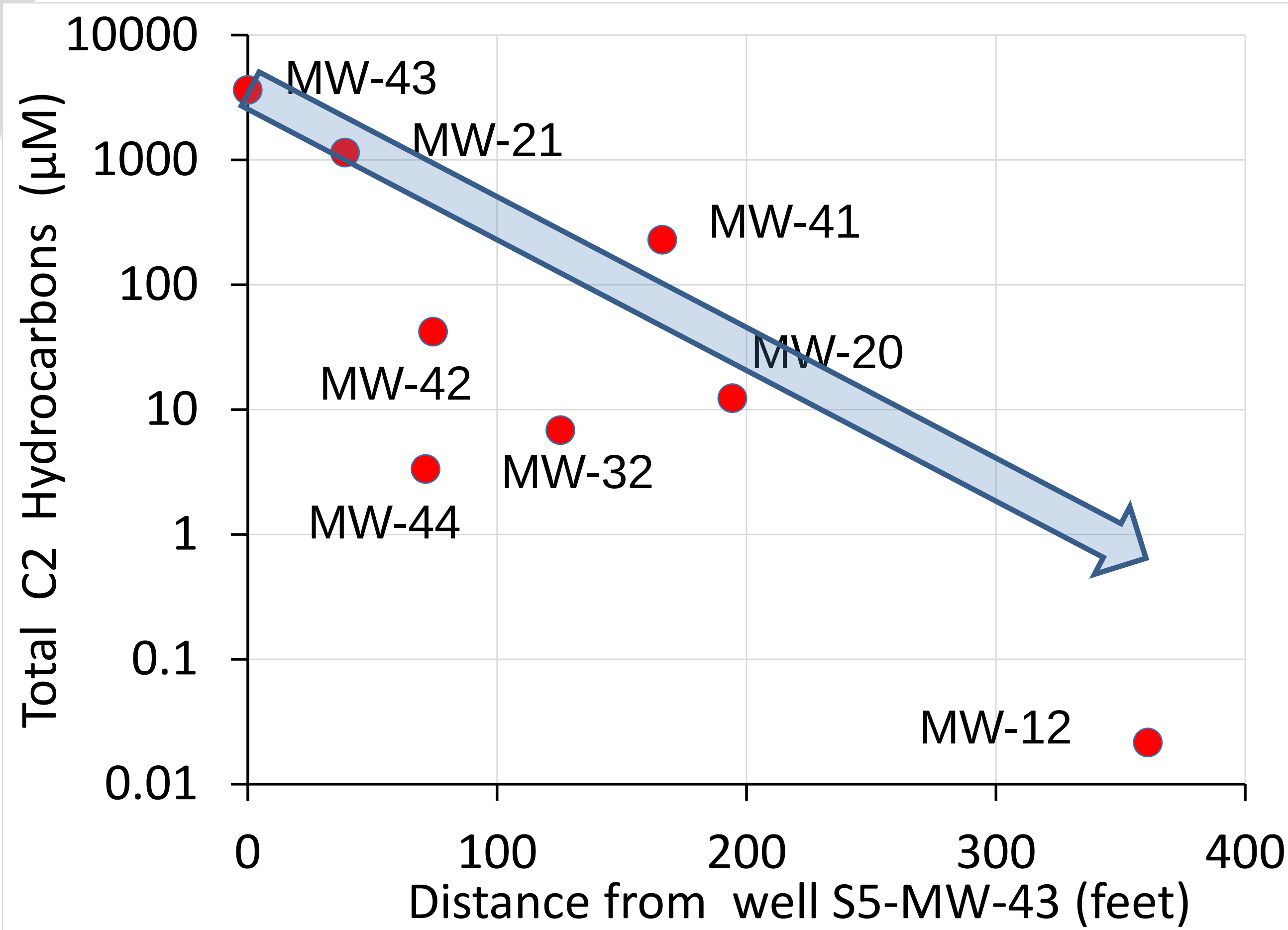
- For purposes of illustration, assume the receptor is the high tide line, which defines the waters of the State of California
- In the absence of biodegradation, would TCE, DCE and Vinyl Chloride reach the receptor at concentrations in excess of the MCL?

500 feet


100 feet
Total Chlorinated Alkenes
Detected
> 100 µg/L
> 10,000 µg/L
> 100,000 µg/L



44
21
43
41
42
32
20
12

Total C2 Hydrocarbons (µM)
10000
1000
100
10
1
0.1
0.01
0
100
200
300
400
Distance from well S5-MW-43 (feet)
MW-43
MW-21
MW-41
MW-20
MW-42
MW-32
MW-44
MW-12

# BIOCHLOR Natural Attenuation Decision Support System

*Version 2.2*

Excel 2000

NAS North Island

Site 5 - Unit 2

Run Name

**Data Input Instructions:**

115 → 1. Enter value directly....or

or 2. Calculate by filling in gray

0.02 cells. Press Enter, then C

(To restore formulas, hit "Restore Formulas" button )

Variable* → Data used directly in model.

Test if Biotransformation is Occurring → Natural Attenuation Screening Protocol

TYPE OF CHLORINATED SOLVENT: Ethenes (selected) / Ethanes

**1. ADVECTION** C

| | | | |
|---|---|---|---|
| Seepage Velocity* | Vs | 163.9 | (ft/yr) |
| *or* | | | |
| Hydraulic Conductivity | K | 9.9E-03 | (cm/sec) |
| Hydraulic Gradient | i | 0.004 | (ft/ft) |
| Effective Porosity | n | 0.25 | (-) |

**2. DISPERSION**

| | | |
|---|---|---|
| Alpha x* | 29.447 | (ft) |
| (Alpha y) / (Alpha x)* | 0.1 | (-) |
| (Alpha z) / (Alpha x)* | 1.E-99 | (-) |

Calc. Alpha x

**3. ADSORPTION** C

Retardation Factor* → R

*or*

| | | |
|---|---|---|
| Soil Bulk Density, rho | 1.4 | (kg/L) |
| FractionOrganicCarbon, foc | 5.0E-3 | (-) |

Partition Coefficient

| | Koc | | R | |
|---|---|---|---|---|
| PCE | 300 | (L/kg) | 9.40 | (-) |
| TCE | 100 | (L/kg) | 3.80 | (-) |
| DCE | 50 | (L/kg) | 2.40 | (-) |
| VC | 3 | (L/kg) | 1.08 | (-) |
| ETH | 1 | (L/kg) | 1.03 | (-) |

**Common R (used in model)* = 2.40**

**4. BIOTRANSFORMATION** -1st Order Decay Coefficient* C

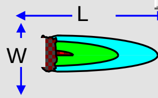
| Zone 1 | λ (1/yr) | half-life (yrs) | Yield |
|---|---|---|---|
| PCE → TCE | 0.000 | | 0.79 |
| TCE → DCE | 0.000 | | 0.74 |
| DCE → VC | 0.000 | | 0.64 |
| VC → ETH | 0.000 | | 0.45 |

| Zone 2 | λ (1/yr) | half-life (yrs) |
|---|---|---|
| PCE → TCE | 0.000 | |
| TCE → DCE | 0.000 | |
| DCE → VC | 0.000 | |
| VC → ETH | 0.000 | |

λ HELP

**5. GENERAL** C

| | | |
|---|---|---|
| Simulation Time* | 33 | (yr) |
| Modeled Area Width* | 500 | (ft) |
| Modeled Area Length* | 1500 | (ft) |
| Zone 1 Length* | 1500 | (ft) |
| Zone 2 Length* | 0 | (ft) |




Zone 2= L - Zone 1

**6. SOURCE DATA** TYPE: Continuous Single Planar

Source Options

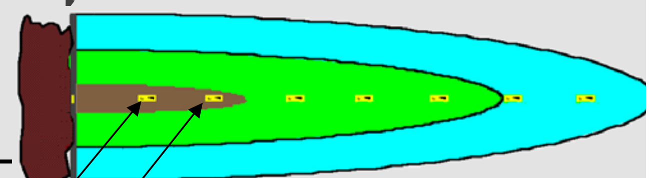
Vertical Plane Source: Determine Source Well Location and Input Solvent Concentrations

Source Thickness in Sat. Zone* 80 (ft)

Y1

Width* (ft) 50

| Conc. (mg/L)* | C1 | $k_s$* (1/yr) |
|---|---|---|
| PCE | | 0 |
| TCE | | 0 |
| DCE | 500.0 | 0 |
| VC | 87.0 | 0 |
| ETH | 0.72 | 0 |



View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

**7. FIELD DATA FOR COMPARISON**

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PCE Conc. (mg/L) | | | | | | | | | | | |
| TCE Conc. (mg/L) | | | | | | | | | | | |
| DCE Conc. (mg/L) | 500.0 | 17.0 | 16.0 | .046 | | | | | | | |
| VC Conc. (mg/L) | 87.0 | 25.0 | 71.0 | .88 | | | | | | | |
| ETH Conc. (mg/L) | 0.7 | 48.0 | 72.0 | 178.0 | | | | | | | |
| Distance from Source (ft) | 0 | 48 | 72 | 178 | | | | | | | |

Date Data Collected 20005 July

**8. CHOOSE TYPE OF OUTPUT TO SEE:**

RUN CENTERLINE | RUN ARRAY | *Help* | Restore | RESET | *SEE OUTPUT* | Paste | Unprotect

# Set rate constants for degradation of DCE to VC and VC to ETH to zero

**4. BIOTRANSFORMATION** **-1st Order Decay Coefficient*** C

**Zone 1**

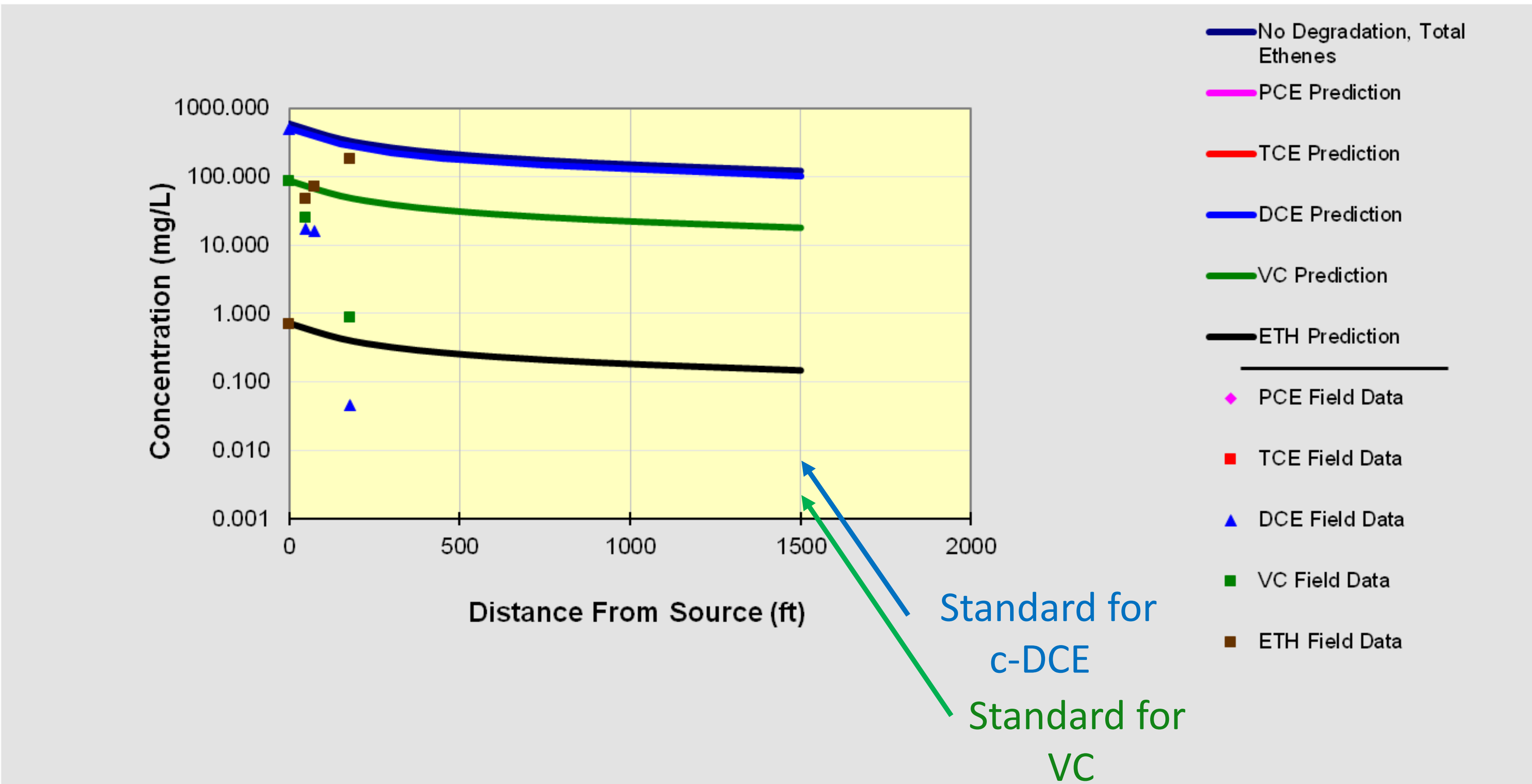
| | λ (1/yr) | half-life (yrs) | Yield |
|---|---|---|---|
| PCE → TCE | 0.000 | | 0.79 |
| TCE → DCE | 0.000 | | 0.74 |
| DCE → VC | 0.000 | | 0.64 |
| VC → ETH | 0.000 | | 0.45 |

**Zone 2**

| | λ (1/yr) | half-life (yrs) |
|---|---|---|
| PCE → TCE | 0.000 | |
| TCE → DCE | 0.000 | |
| DCE → VC | 0.000 | |
| VC → ETH | 0.000 | |

**λ HELP**

# Dissolved Chlorinated Solvent Concentrations Along Plume Centerline



# Optimum Rate Constants for Degradation of DCE to VC and VC to ETH

**4. BIOTRANSFORMATION** **-1st Order Decay Coefficient*** C

**Zone 1**

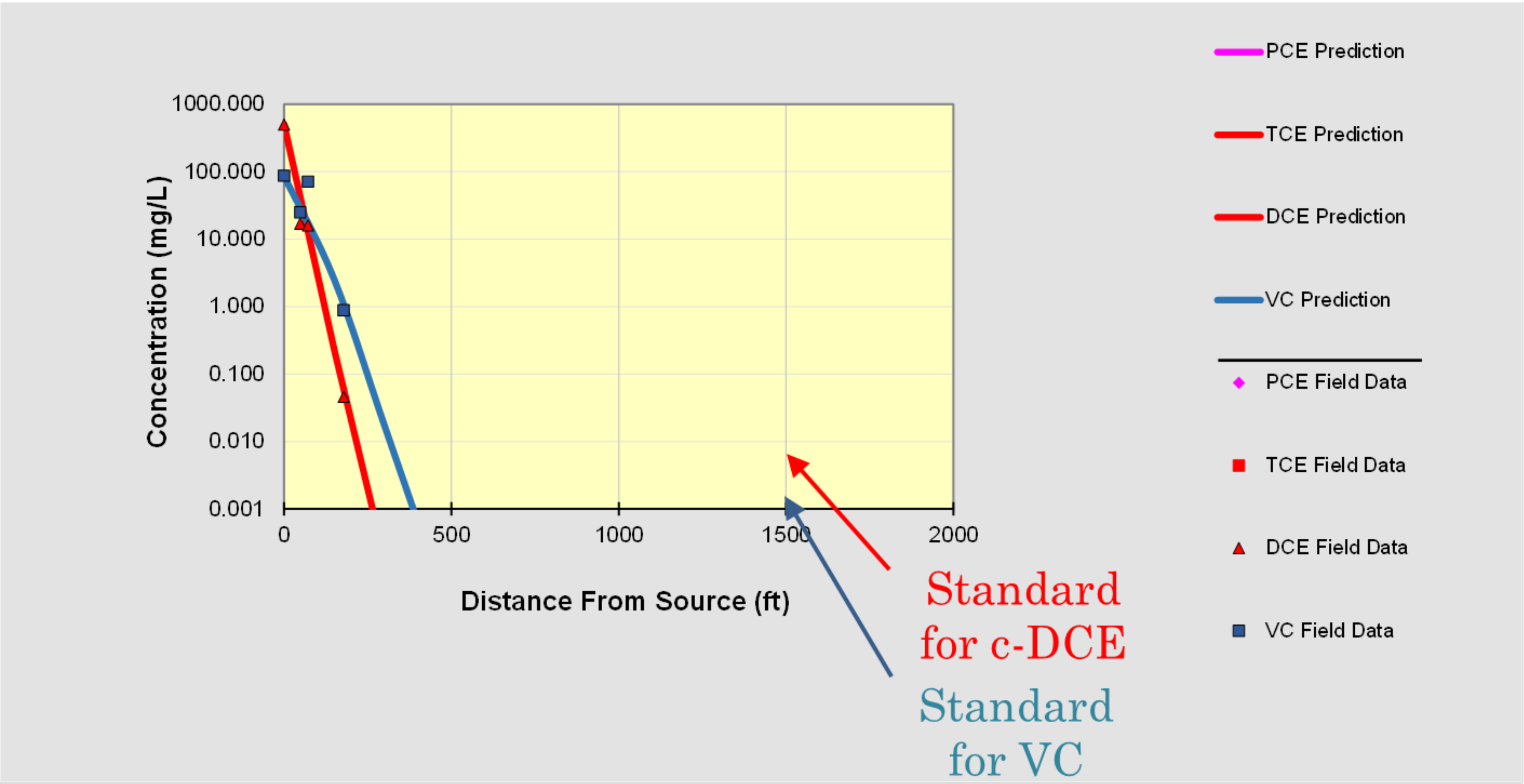
| Reaction | λ (1/yr) | half-life (yrs) | Yield |
|---|---|---|---|
| PCE → TCE | 0.000 | | 0.79 |
| TCE → DCE | 0.000 | | 0.74 |
| DCE → VC | 17.000 | | 0.64 |
| VC → ETH | 10.000 | | 0.45 |

**Zone 2**

| Reaction | λ (1/yr) | half-life (yrs) |
|---|---|---|
| PCE → TCE | 0.000 | |
| TCE → DCE | 0.000 | |
| DCE → VC | 0.000 | |
| VC → ETH | 0.000 | |

λ HELP

# Dissolved Chlorinated Solvent Concentrations Along Plume Centerline



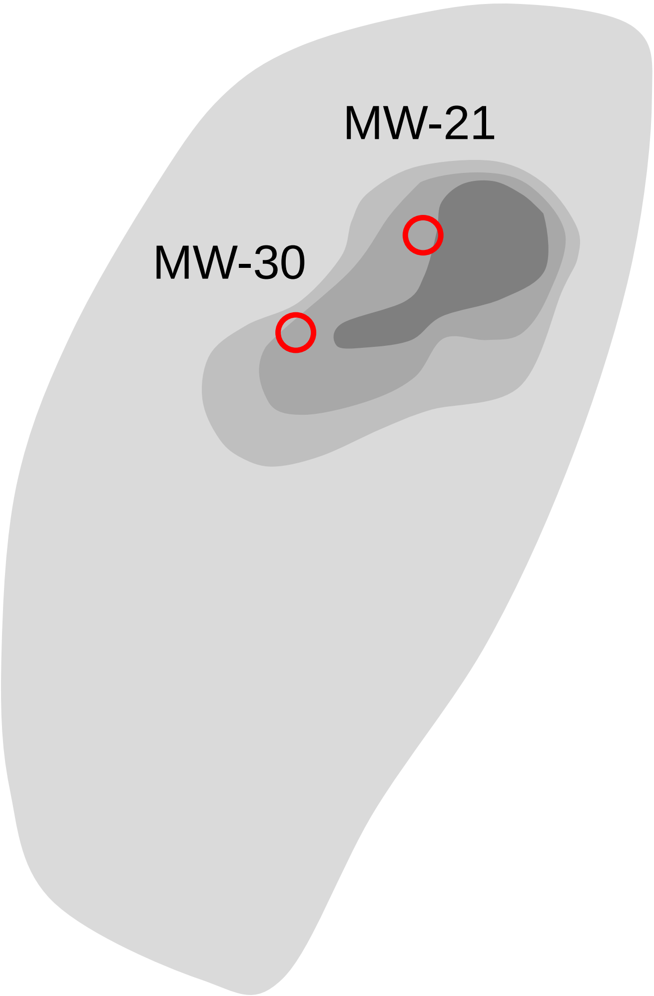
# Is the Rate of Degradation of DCE and VC Adequate?

- Based on the monitoring data and geo-hydrological data as evaluated with BIOCHLOR, natural attenuation can be expected to keep the concentrations of DCE and VC below the regulatory standard at the receptor
- Can we explain the removals of DCE and VC?

# <u>CASE STUDY</u>

## USE OF QPCR FOR GENE COPIES OF *DEHALOCOCCOIDES* BACTERIA TO BOUND THE RATE OF BIOLOGICAL REDUCTIVE DECHLORINATION

Installation Restoration Site 5-Unit 2 (Golf Course Disposal Area), North Island Naval Air Station, San Diego, California




10-6-2005

Density of Dhc 16s ribosomal DNA
Gene Copies per Liter

MW-21 has 6.15E + 09

MW-30 has 3.47E + 08

WATER RESEARCH 40 (2006) 3131–3140

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

# Relationship between *Dehalococcoides* DNA in ground water and rates of reductive dechlorination at field scale

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[b]*US Environmental Protection Agency, 919 Kerr Research Drive, Ada, OK 74820, USA*

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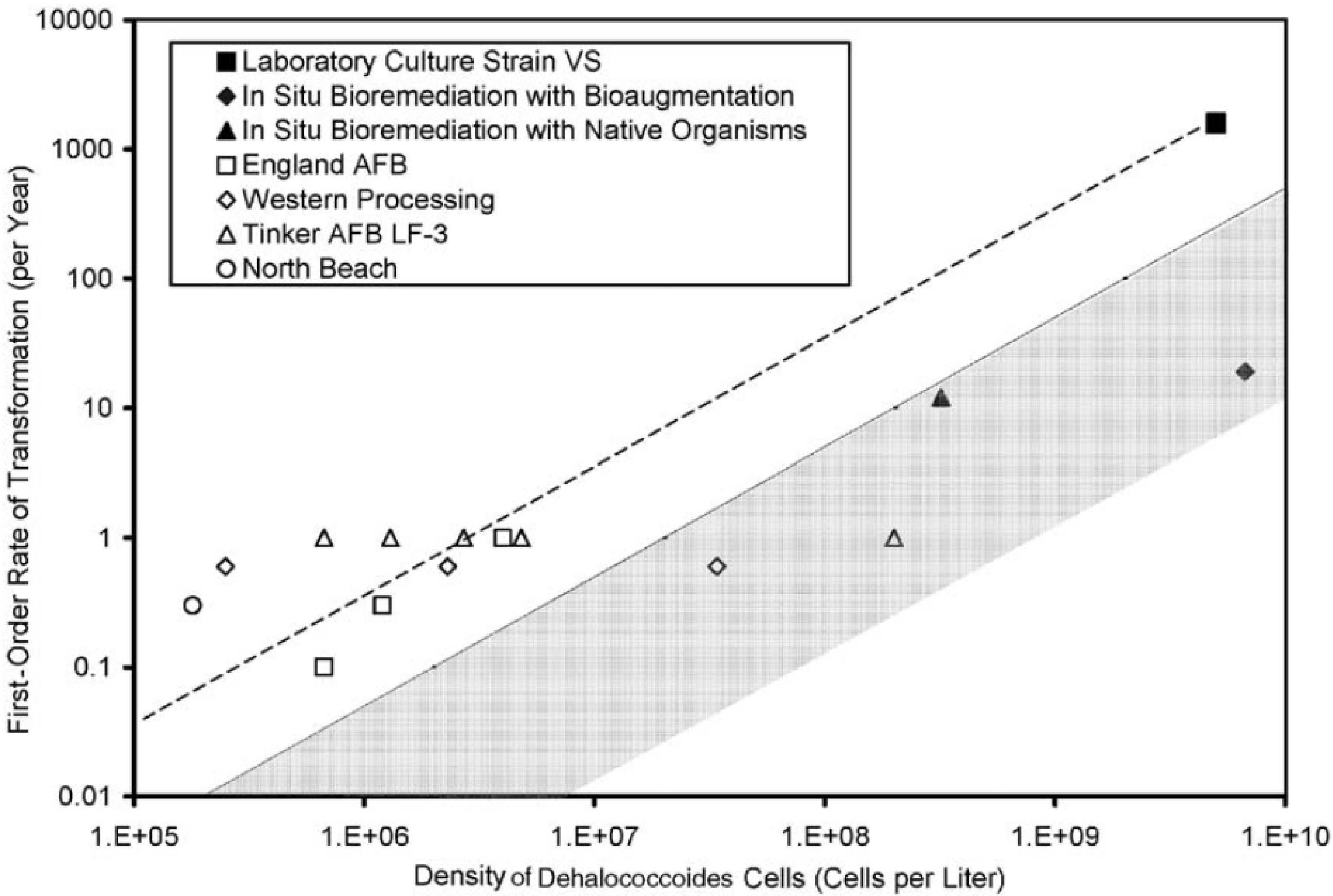
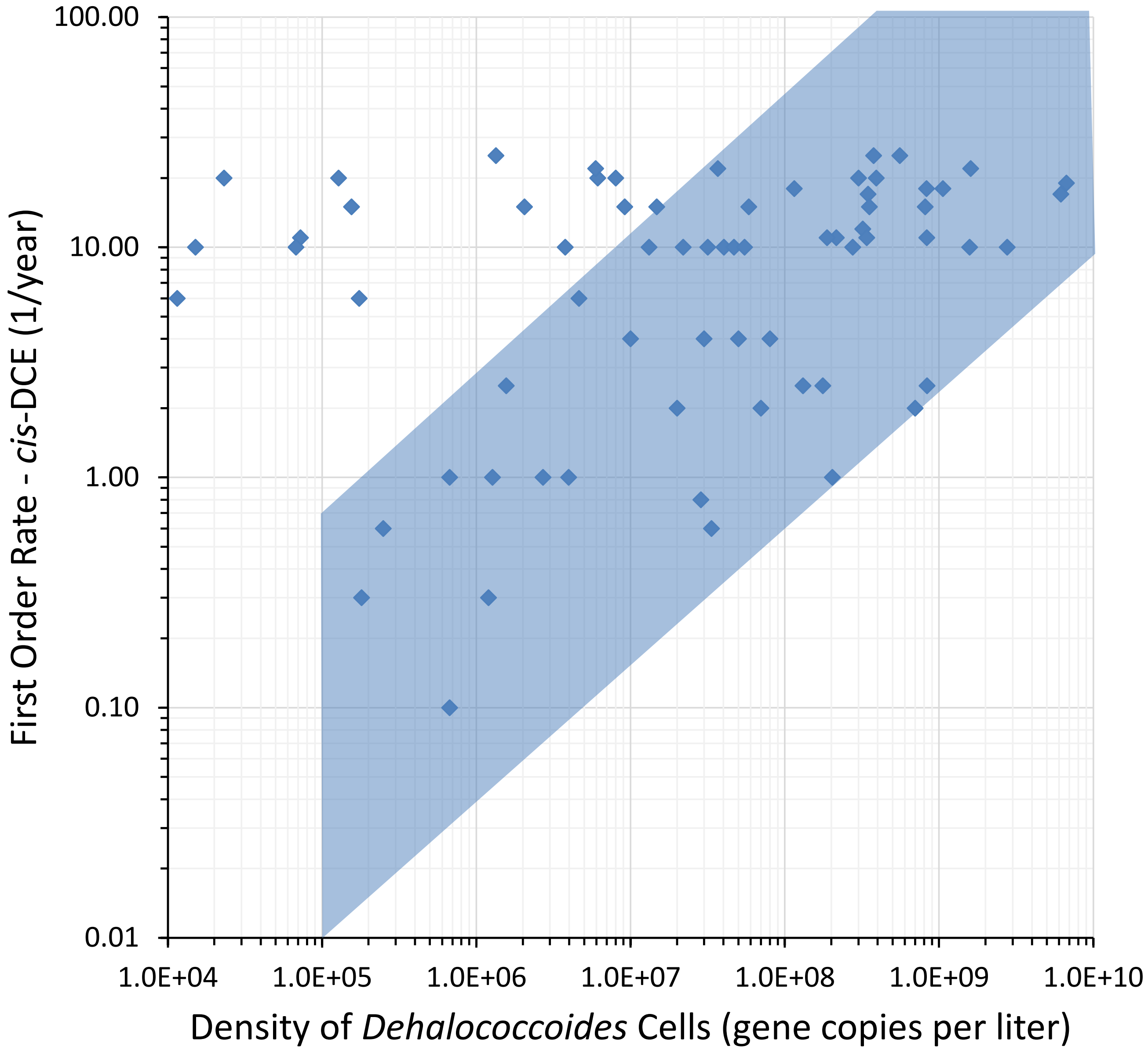
*Dehalococcoides* DNA
Rate constants
Reductive dechlorination
Natural attenuation

ABSTRACT

Certain strains of *Dehalococcoides* bacteria can dechlorinate chlorinated ethylenes to harmless products. This study was conducted to determine if there is a valid association between the density of *Dehalococcoides* DNA in ground water and the observed rates of reductive dechlorination at field scale. *Dehalococcoides* DNA in water from monitoring wells was determined using the quantitative real time polymerase chain reaction (q-PCR) with DNA primer set specific for *Dehalococcoides* organisms. Dechlorination rate constants were extracted from field data using the BIOCHLOR software. Of the six conventional plumes surveyed, "generally useful" rates of dechlorination (greater than or equal to 0.3 per year) of *cis*-dichloroethylene (*cis*-DCE) and vinyl chloride (VC) along the flow path were observed at three sites where *Dehalococcoides* DNA was detected, and little attenuation of *cis*-DCE and VC occurred at two sites where *Dehalococcoides* DNA was not detected. At the two sites where there was no net direction of ground water flow, the relationship between the density of *Dehalococcoides* DNA in ground water and the trend in concentrations of chlorinated ethylenes over time in monitoring wells was not so consistent as that observed for the conventional plumes. A comparison of our study to a field study performed by Lendvay and his coworker indicated that monitoring wells did not efficiently sample the *Dehalococcoides* organisms in the aquifer.

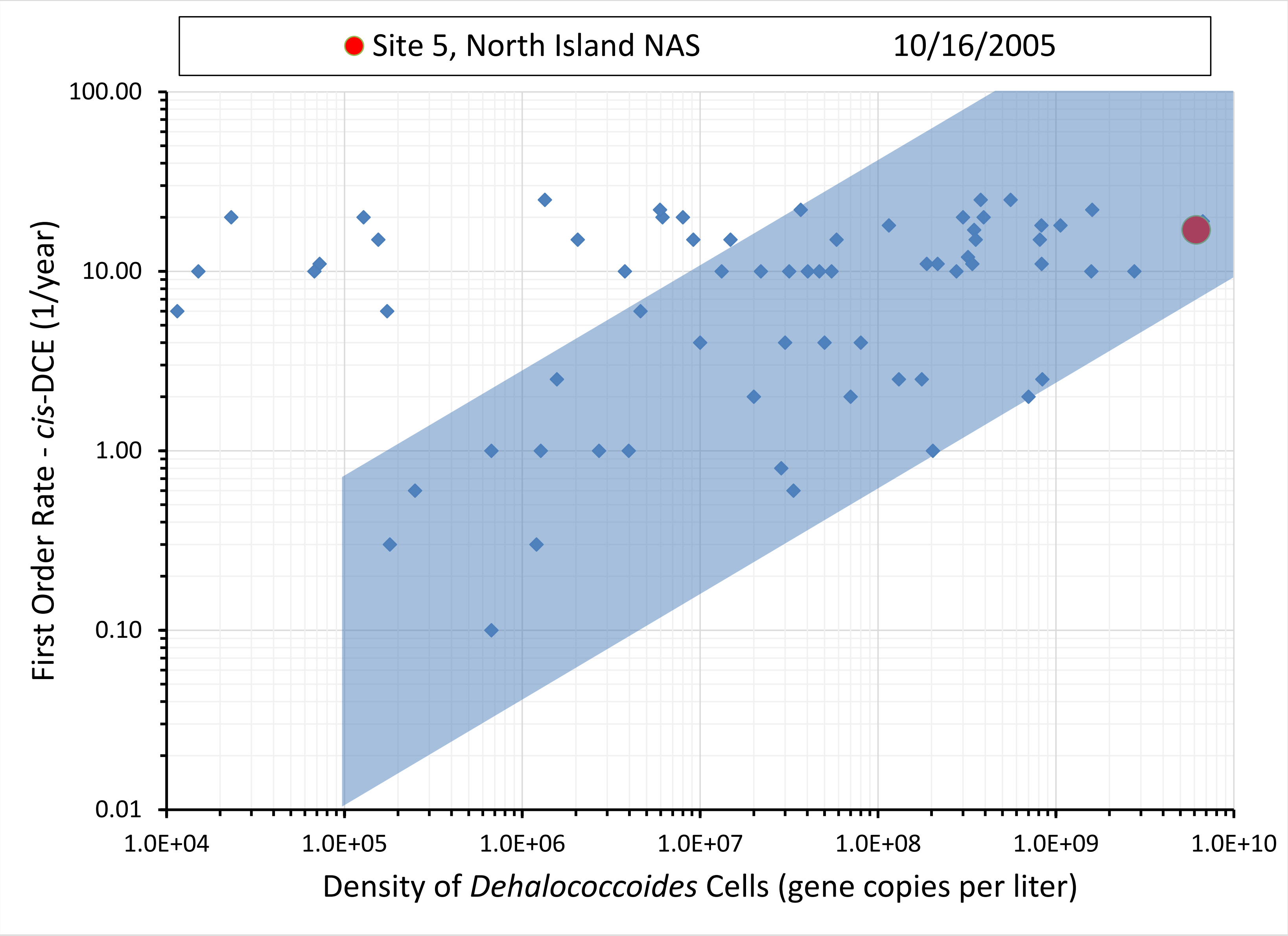


10000
1000
100
10
1
0.1
0.01
First-Order Rate of Transformation (per Year)
Laboratory Culture Strain VS
In Situ Bioremediation with Bioaugmentation
In Situ Bioremediation with Native Organisms
England AFB
Western Processing
Tinker AFB LF-3
North Beach
1.E+05
1.E+06
1.E+07
1.E+08
1.E+09
1.E+10
Density of Dehalococcoides Cells (Cells per Liter)

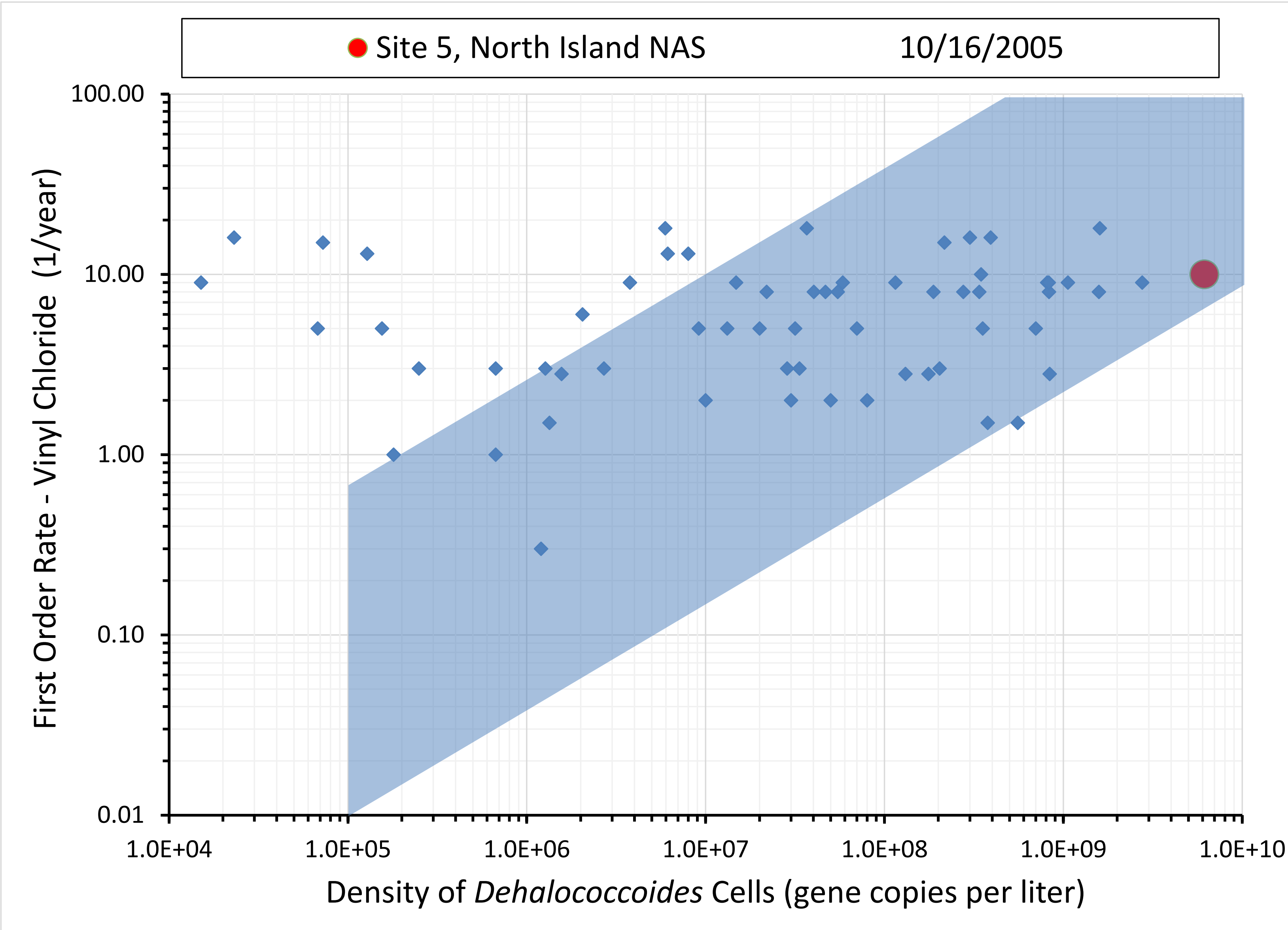


100.00
10.00
1.00
0.10
0.01
1.0E+04
1.0E+05
1.0E+06
1.0E+07
1.0E+08
1.0E+09
1.0E+10
First Order Rate - *cis*-DCE (1/year)
Density of *Dehalococcoides* Cells (gene copies per liter)

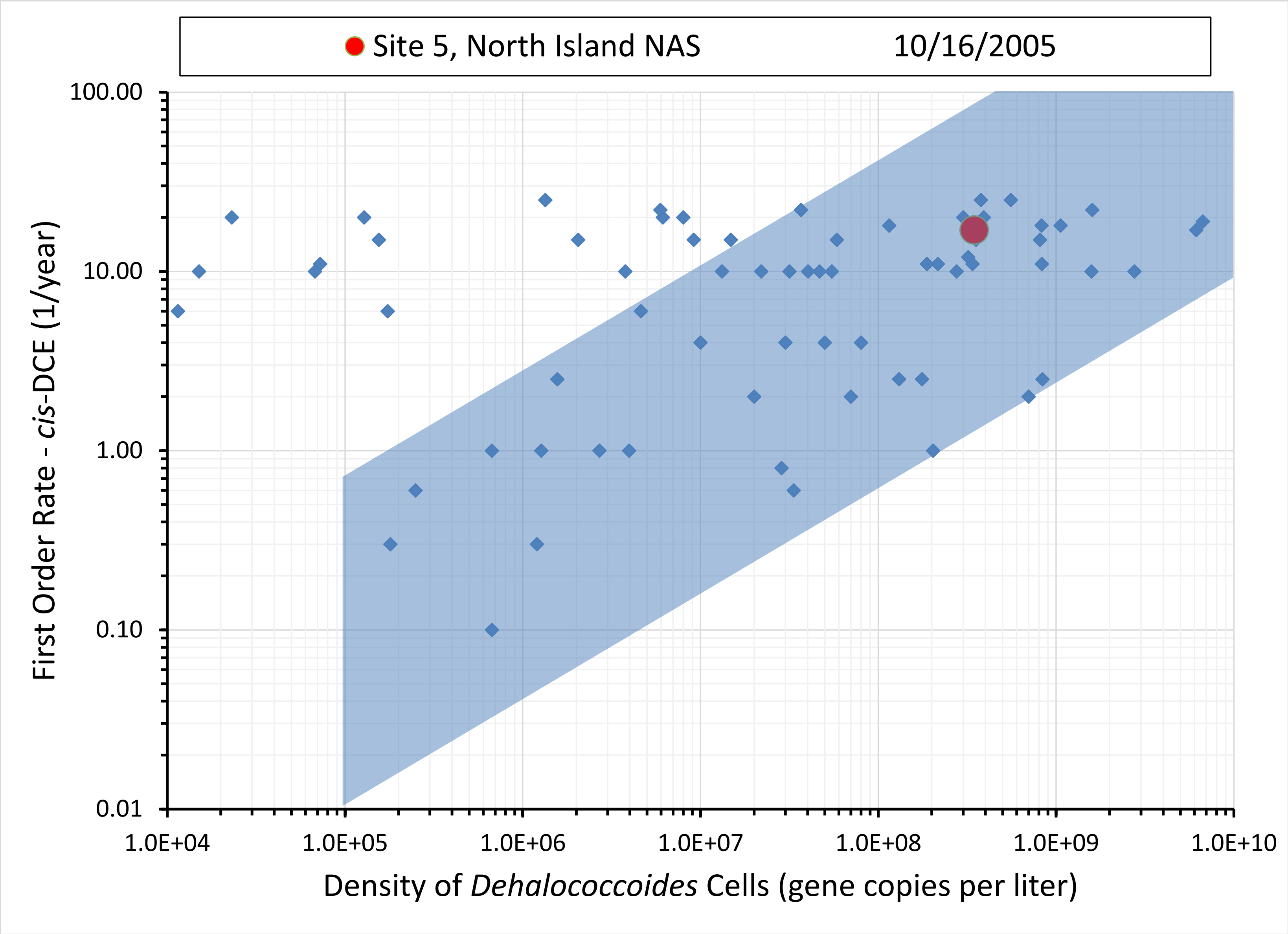
| | | |
|---|---|---|
| | **Overwrite input cells with data specific to your site** | The BASELINE rate constant is the slowest rate constant that is plausibly associated with *Dehalococcoides* DNA (*Dhc*) |
| | Input | |
| | First order rate constant for degradation per year | Fraction of rate constants in the benchmark data set that exceed the BASELINE to a extent than this rate constant |
| *cis*-DCE | 17 | >80% |
| Vinyl Chloride | 10 | >80% |
| | qPCR assay Gene copies per liter | |
| *Dehalococcoides* 16s rRNA | 6.15E+09 | |
| Location and Site | Site 5, North Island NAS | |
| Date | 10/16/2005 | |



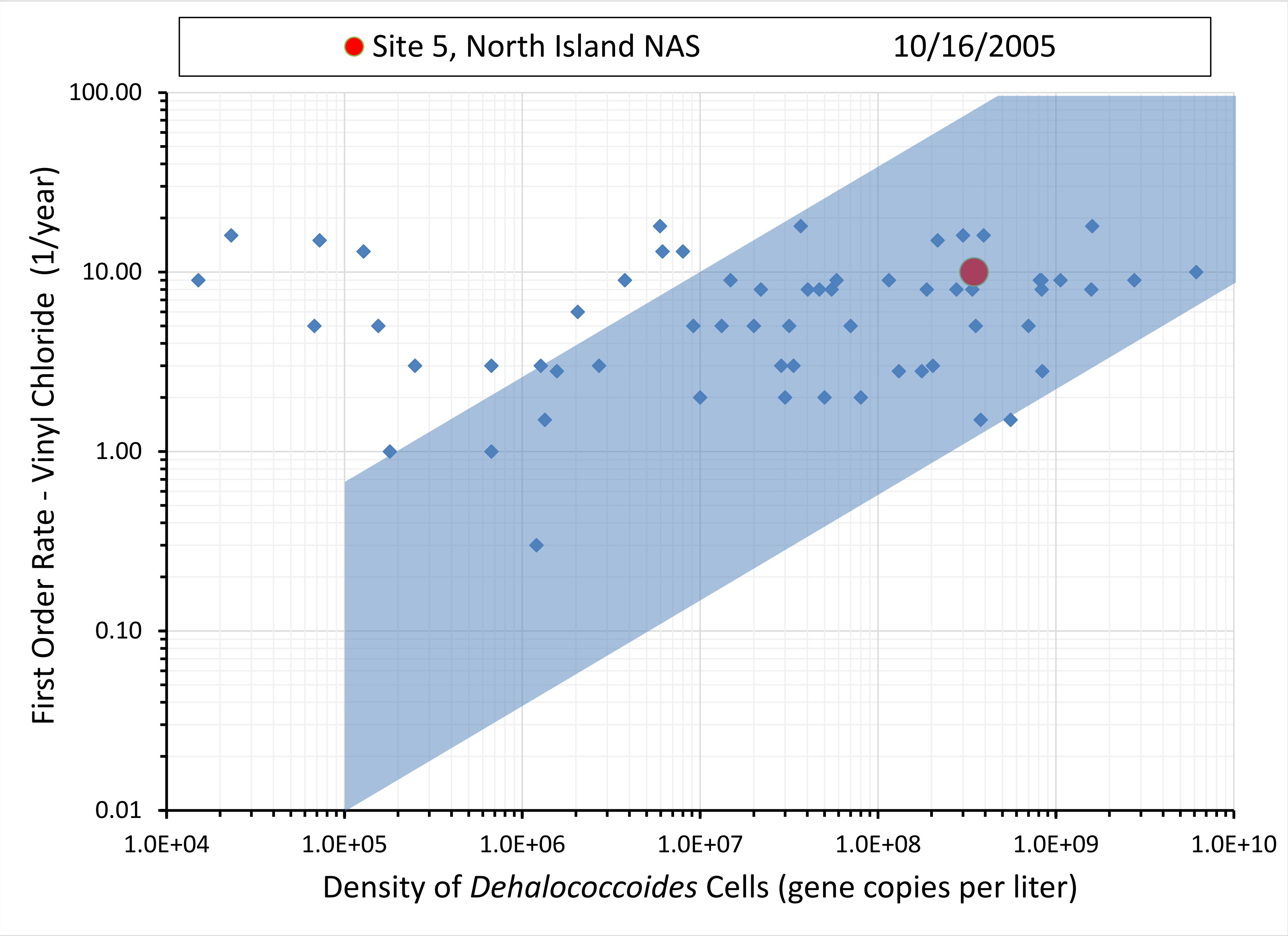
Site 5, North Island NAS
10/16/2005
100.00
10.00
1.00
0.10
0.01
First Order Rate - *cis*-DCE (1/year)
1.0E+04
1.0E+05
1.0E+06
1.0E+07
1.0E+08
1.0E+09
1.0E+10
Density of *Dehalococcoides* Cells (gene copies per liter)


Site 5, North Island NAS
10/16/2005
100.00
10.00
1.00
0.10
0.01
First Order Rate - Vinyl Chloride (1/year)
1.0E+04
1.0E+05
1.0E+06
1.0E+07
1.0E+08
1.0E+09
1.0E+10
Density of *Dehalococcoides* Cells (gene copies per liter)

| | | |
|---|---|---|
| | **Overwrite input cells with data specific to your site** | The BASELINE rate constant is the slowest rate constant that is plausibly associated |
| | Input | with *Dehalococcoides* DNA (*Dhc*) |
| | | |
| | First order rate constant for degradation per year | Fraction of rate constants in the benchmark data set that exceed the BASELINE to a extent than this rate constant |
| | | |
| *cis*-DCE | 17 | >40% |
| Vinyl Chloride | 10 | >40% |
| | | |
| | qPCR assay Gene copies per liter | |
| | | |
| *Dehalococcoides* 16s rRNA | 3.47E+08 | |
| | | |
| Location and Site | Site 5, North Island NAS | |
| Date | 10/16/2005 | |



Site 5, North Island NAS
10/16/2005
First Order Rate - cis-DCE (1/year)
100.00
10.00
1.00
0.10
0.01
1.0E+04
1.0E+05
1.0E+06
1.0E+07
1.0E+08
1.0E+09
1.0E+10
Density of Dehalococcoides Cells (gene copies per liter)



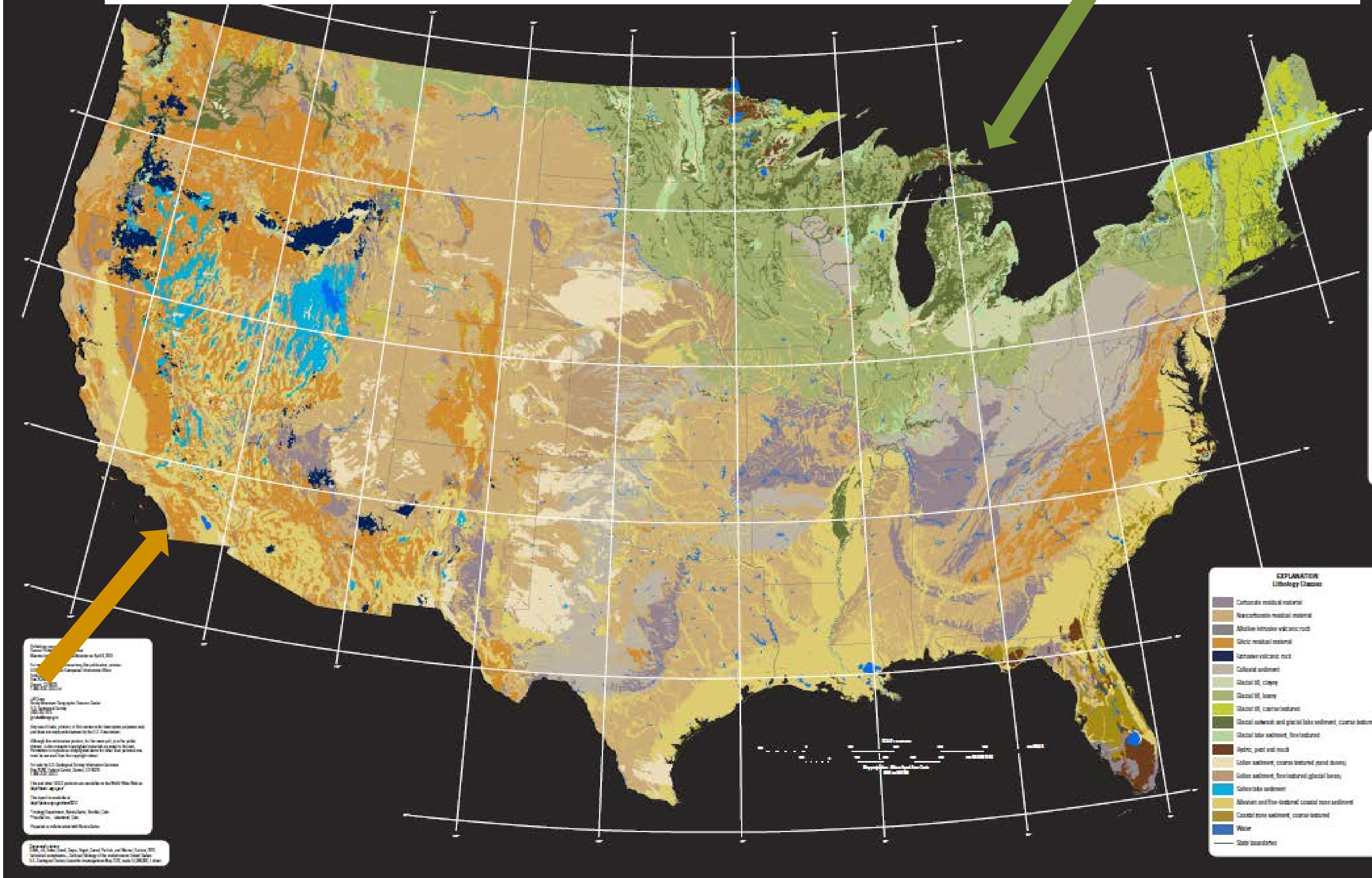
Site 5, North Island NAS
10/16/2005
First Order Rate - Vinyl Chloride (1/year)
100.00
10.00
1.00
0.10
0.01
1.0E+04
1.0E+05
1.0E+06
1.0E+07
1.0E+08
1.0E+09
1.0E+10
Density of *Dehalococcoides* Cells (gene copies per liter)

# Contribution of Magnetite to Abiotic Degradation

- Magnetite ($FeO.Fe_2O_3$) often occurs naturally in sediments formed by weathering of igneous or metamorphic rock
- Magnetite can also be produced in situ by iron-reducing bacteria
- Magnetite can degrade TCE or *cis*-DCE or Vinyl Chloride to oxidized products under either aerobic or anaerobic conditions
- If the TCE or *cis*-DCE is degraded by magnetite, there is no production of Vinyl Chloride

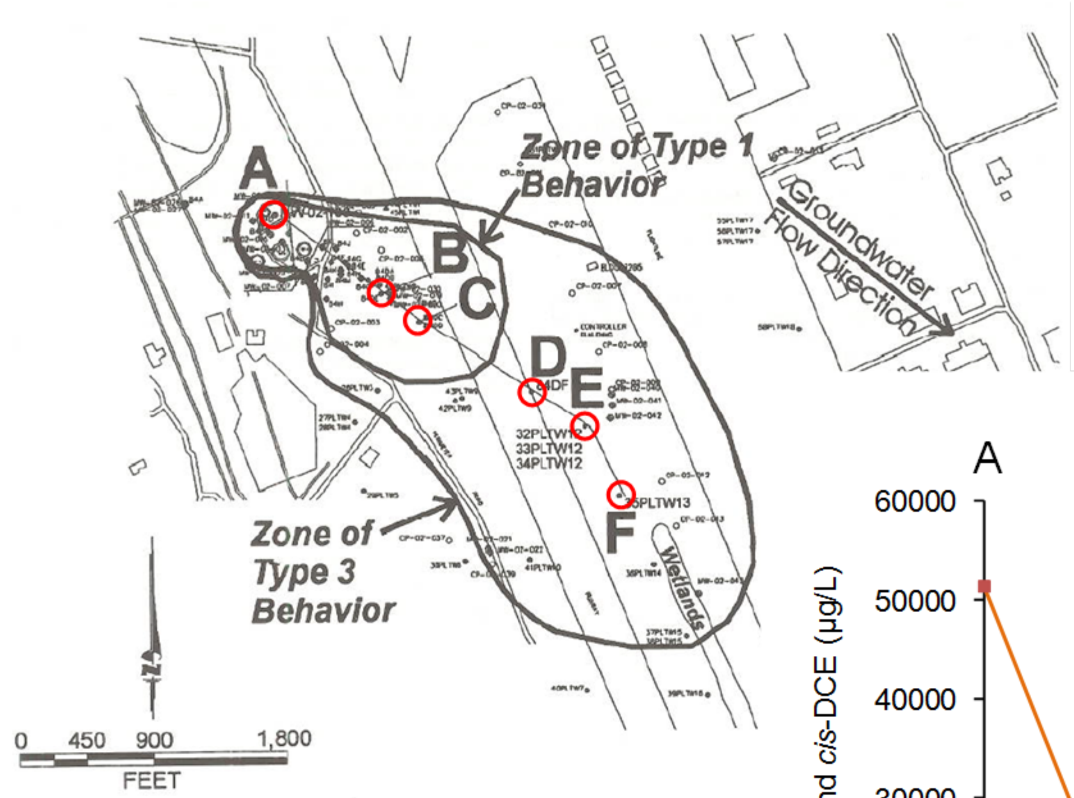
# Sediment from Tooele Army Depot

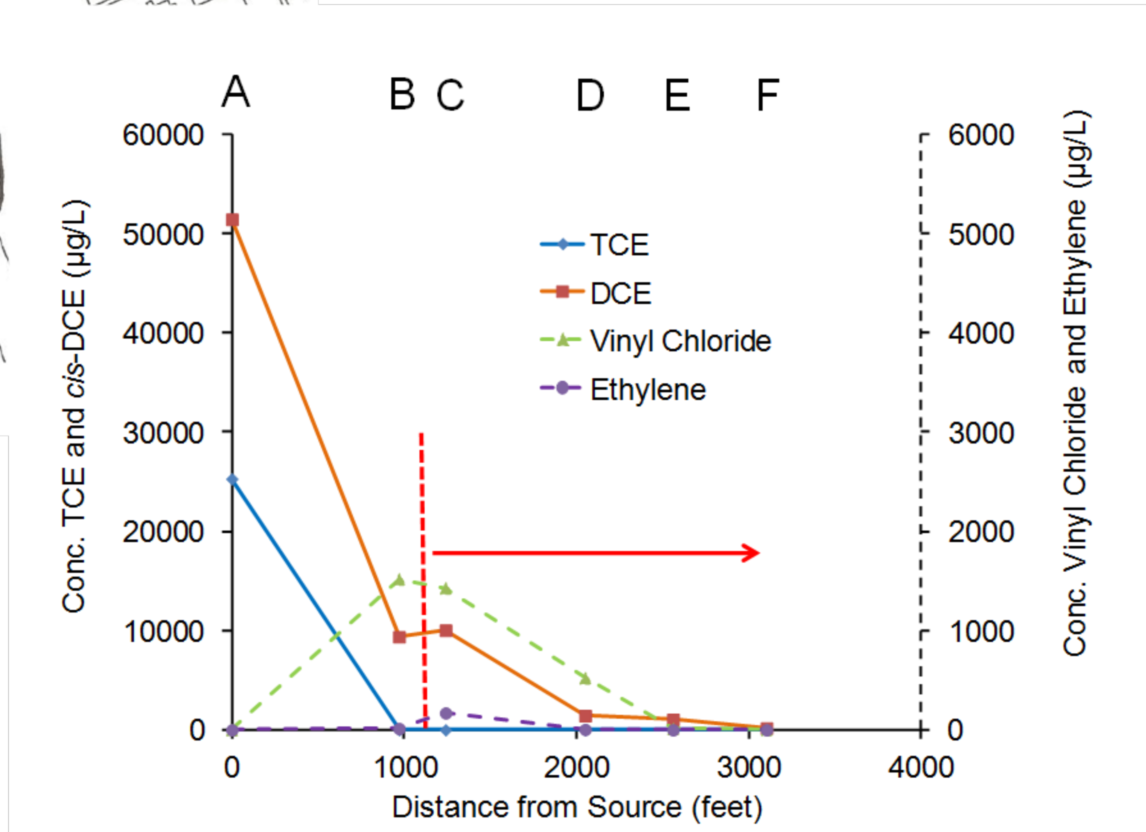
# Terrestrial Ecosystems—Surficial Lithology of the Conterminous United States
http://pubs.usgs.gov/sim/3126/



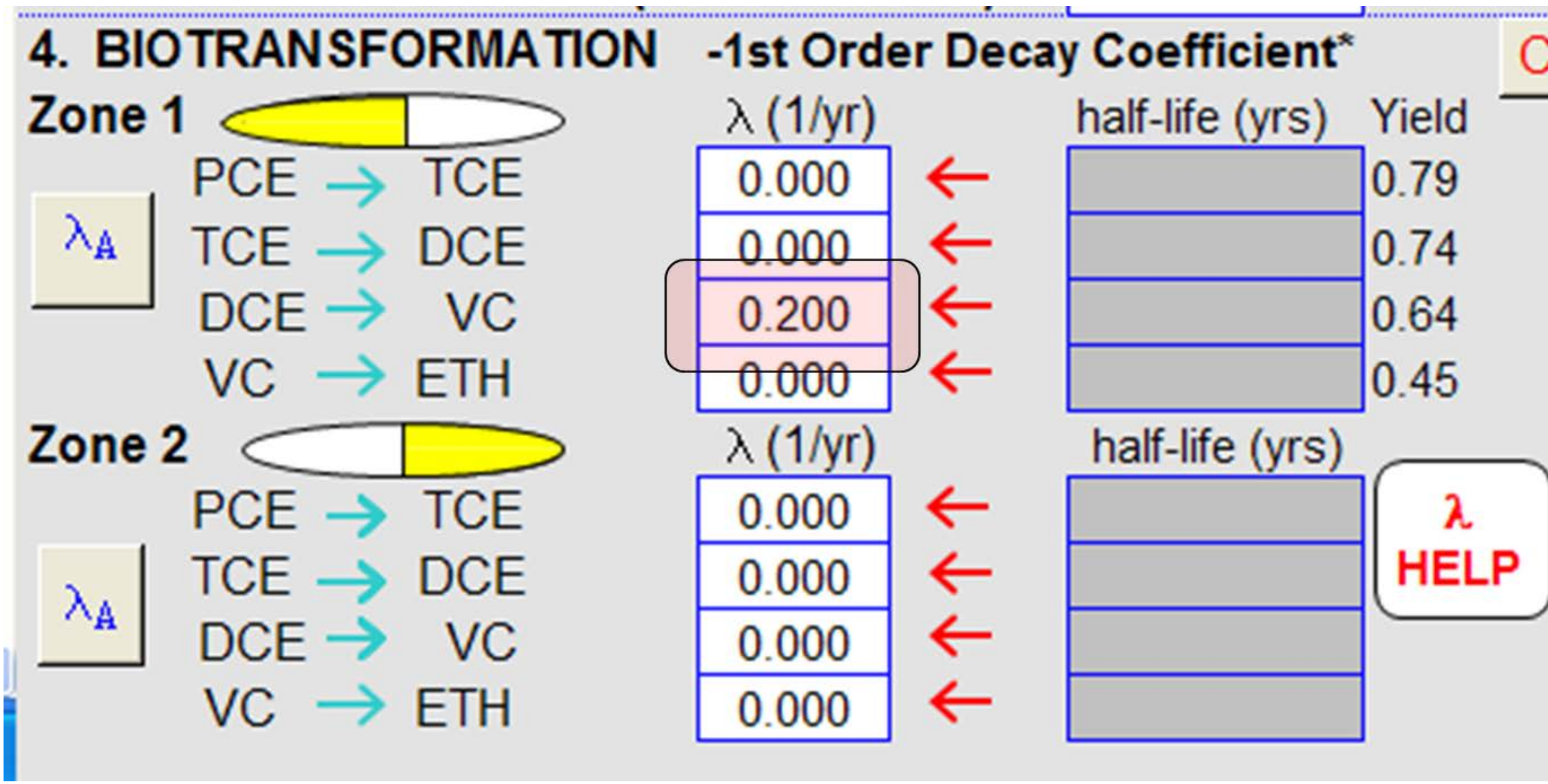
# CASE STUDY
# ABIOTIC DEGRADATION

Large plume originating at a fire protection training facility on the former Plattsburgh AFB, New York


A
B
C
D
E
F
Zone of Type 1 Behavior
Groundwater Flow Direction
Zone of Type 3 Behavior
Wetlands
32PLTW12
33PLTW12
34PLTW12
35PLTW13
0 450 900 1,800
FEET


A B C D E F
Conc. TCE and cis-DCE (µg/L)
Conc. Vinyl Chloride and Ethylene (µg/L)
TCE
DCE
Vinyl Chloride
Ethylene
60000
50000
40000
30000
20000
10000
0
6000
5000
4000
3000
2000
1000
0
0 1000 2000 3000 4000
Distance from Source (feet)

# DCE set to 0.2 per year



# Special Case for Abiotic Degradation

- BIOCHLOR models the degradation of TCE to produce DCE, and the degradation of DCE to produce Vinyl Chloride
- Magnetite does not degrade DCE to Vinyl Chloride
- To model the degradation of Vinyl Chloride, it is also necessary to ignore the concentrations of the DCE in the source well

DCE is not made available to the model to produce more Vinyl Chloride

## 6. SOURCE DATA

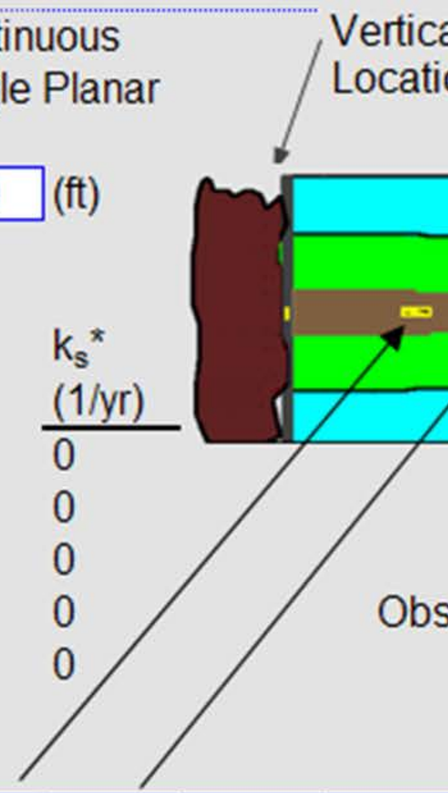
TYPE: Continuous Single Planar

Source Options

Source Thickness in Sat. Zone* 30 (ft)

| | Y1 |
|---|---|
| Width* (ft) | 200 |

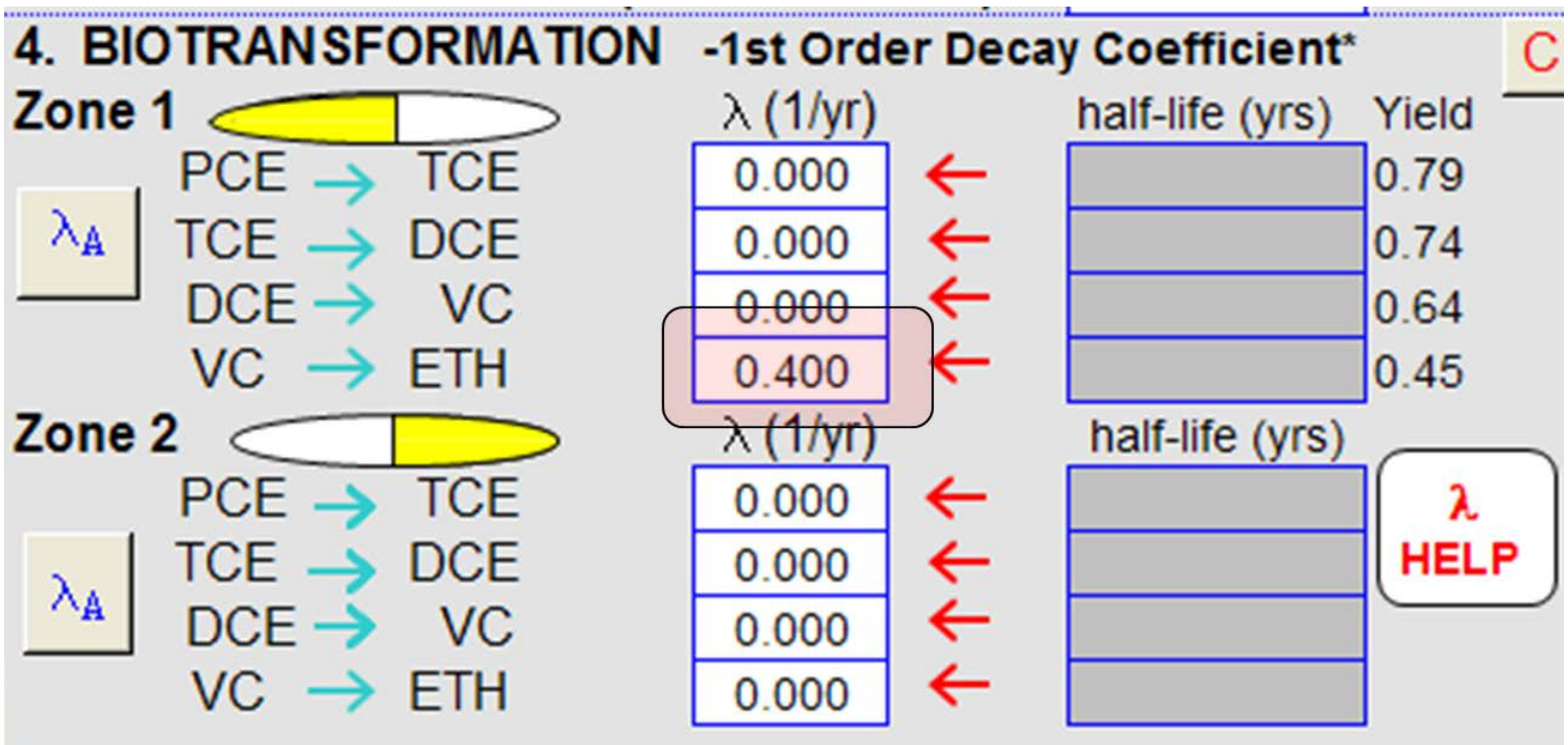
| Conc. (mg/L)* | C1 | $k_s$* (1/yr) |
|---|---|---|
| PCE | | 0 |
| TCE | | 0 |
| DCE | | 0 |
| VC | 1.05 | 0 |
| ETH | 0.17 | 0 |



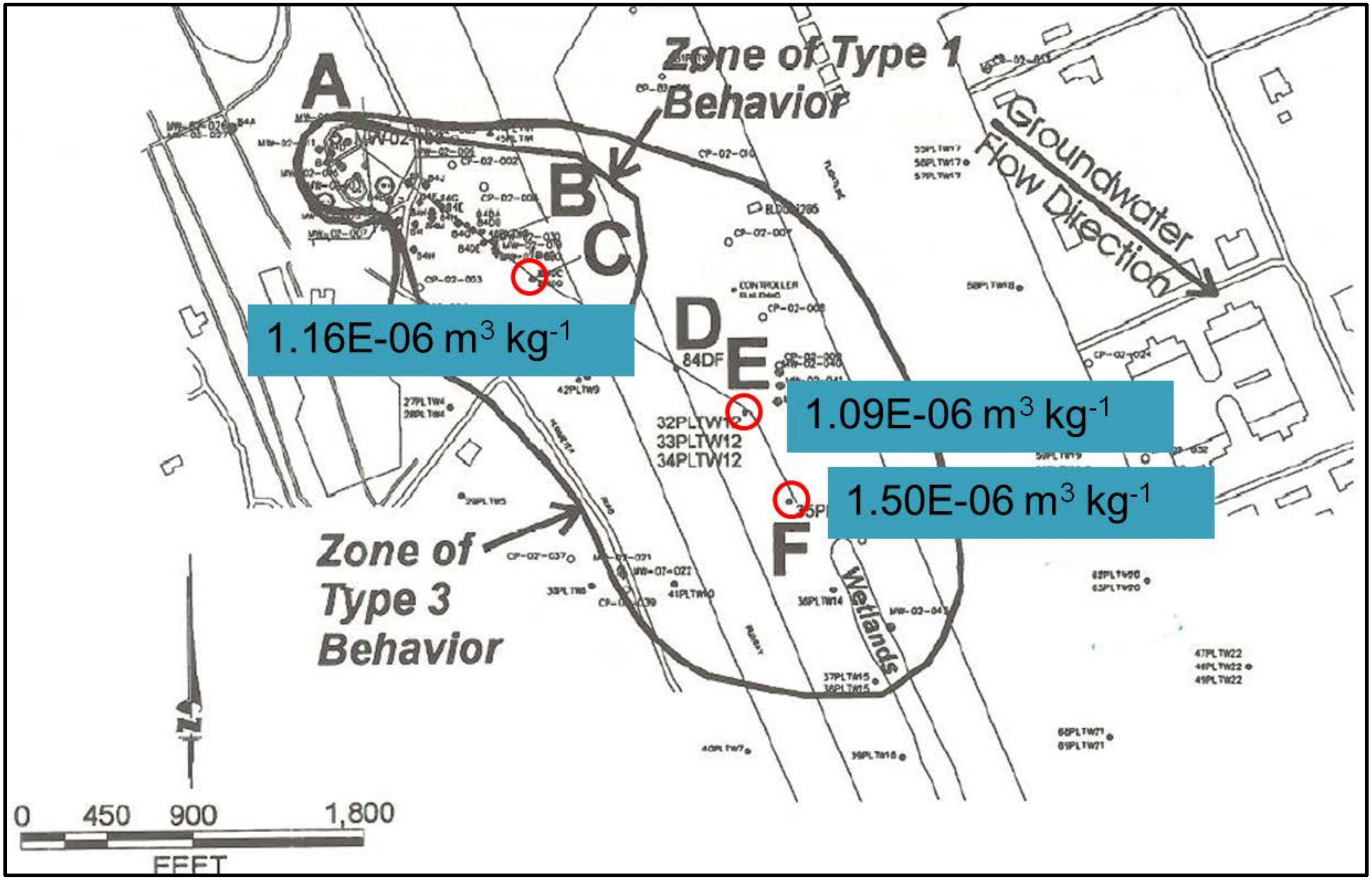

## 7. FIELD DATA FOR COMPARISON

| | | | | | |
|---|---|---|---|---|---|
| PCE Conc. (mg/L) | | | | | |
| TCE Conc. (mg/L) | | | | | |
| DCE Conc. (mg/L) | 10.32 | 1.42 | 1.05 | .177 | |
| VC Conc. (mg/L) | 1.05 | .524 | .012 | .004 | |
| ETH Conc. (mg/L) | .17 | .004 | .001 | .001 | |
| Distance from Source (ft) | 0 | 810 | 1320 | 1863 | |
| Date Data Collected | 1996 | | | | |

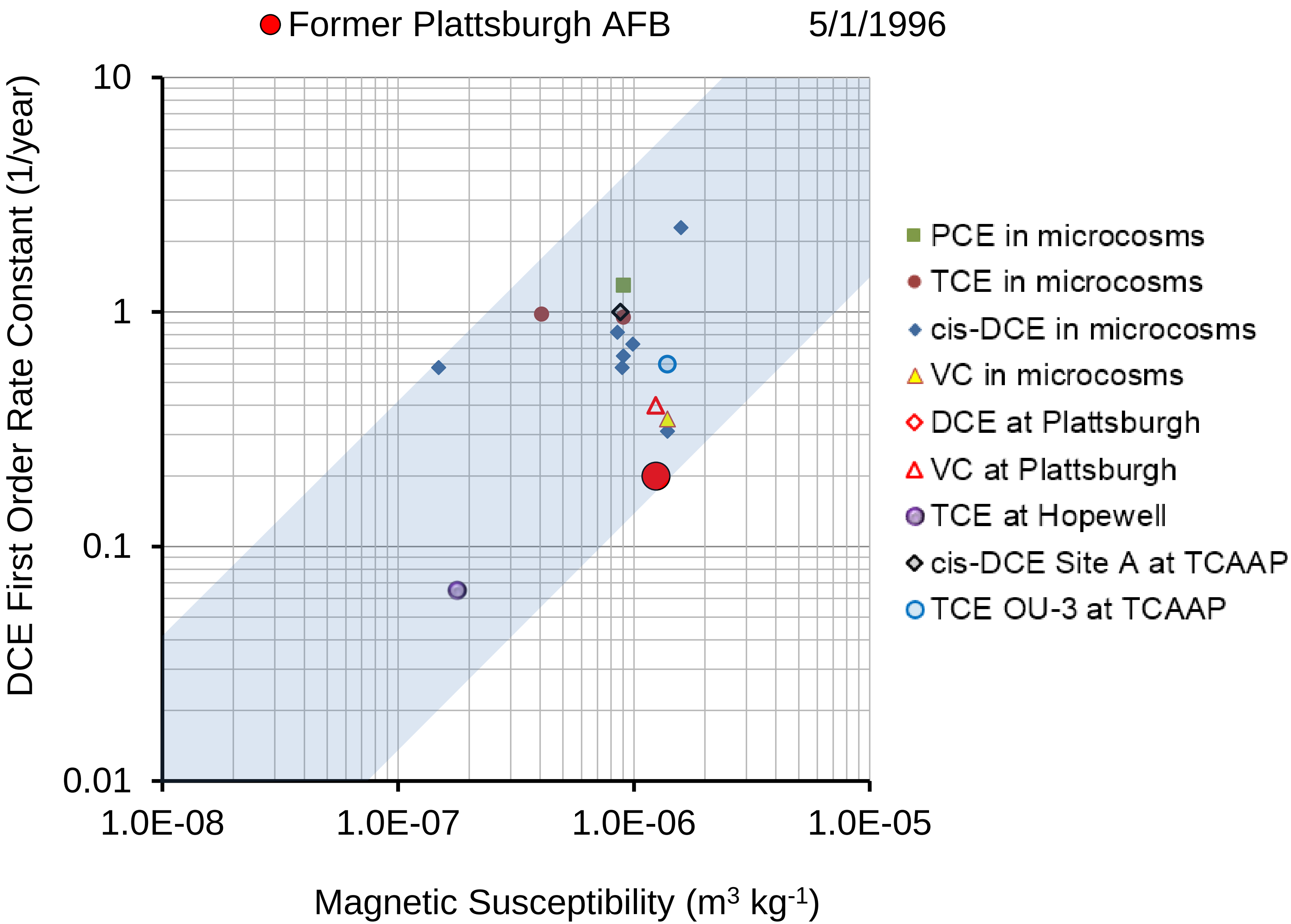
# Vinyl Chloride rate constant set to 0.4 per year

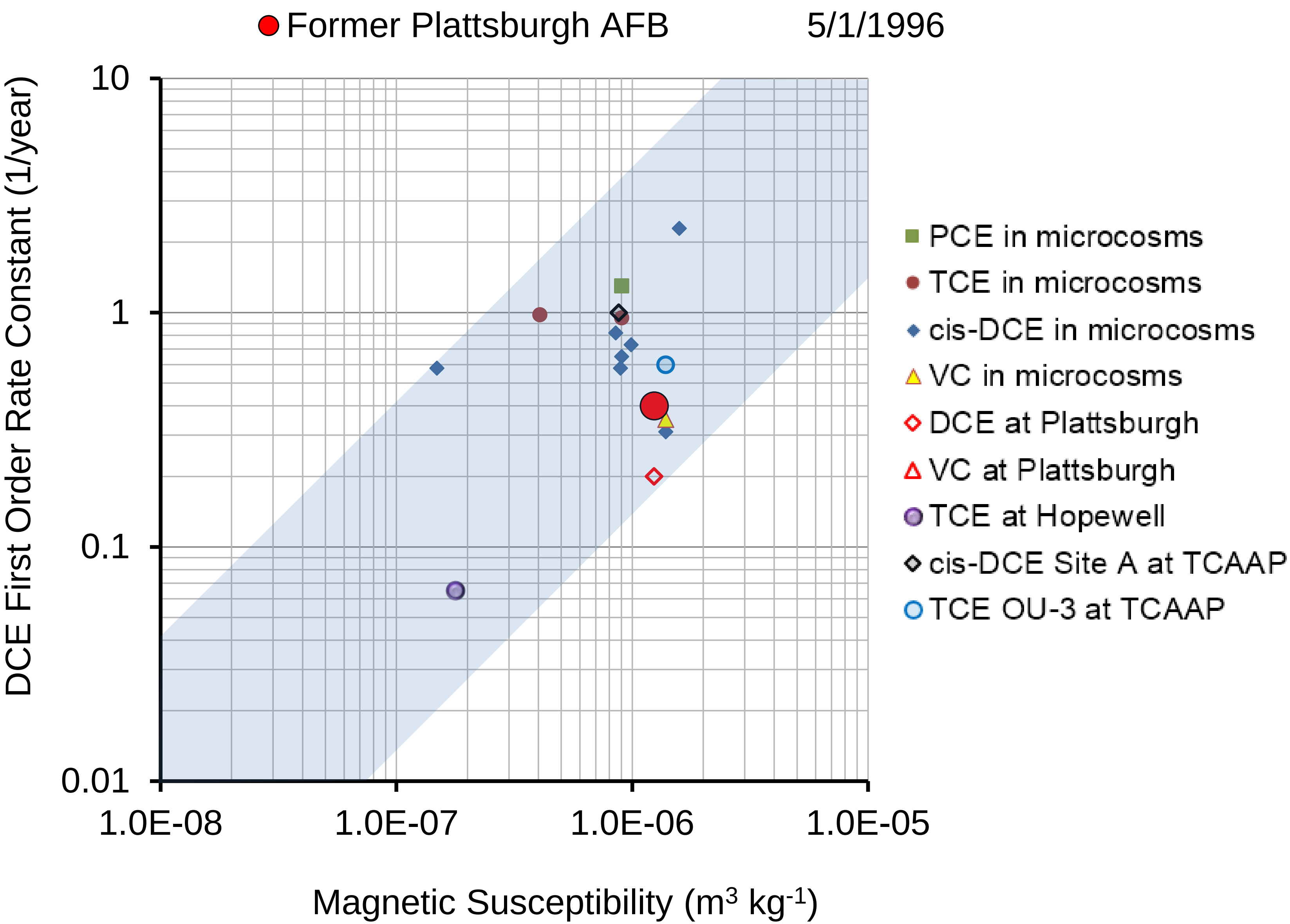


# Average Magnetic Susceptibility of Sediment Samples



| | | |
|---|---|---|
| | **Overwrite input cells with data specific to your site** | The BASELINE is the lower boundary of the blue shape that encompases plausibe rate constants associated with degradation on magnetite |
| | Input | |
| | First order rate constant for degradation per year | Fraction of rate constants in the benchmark data set that exceed the BASELINE to a greater extent than this rate constant |
| PCE | | rate slower than expected |
| TCE | | rate slower than expected |
| cis-DCE | 0.2 | >80% |
| Vinyl Chloride | 0.4 | >60% |
| | Magnetic Suceptibility SI Units ($m^3kg^{-1}$) | |
| | 1.25E-06 | |
| Location and Site | Former Plattsburgh AFB | |
| Date | 5/1/1996 | |

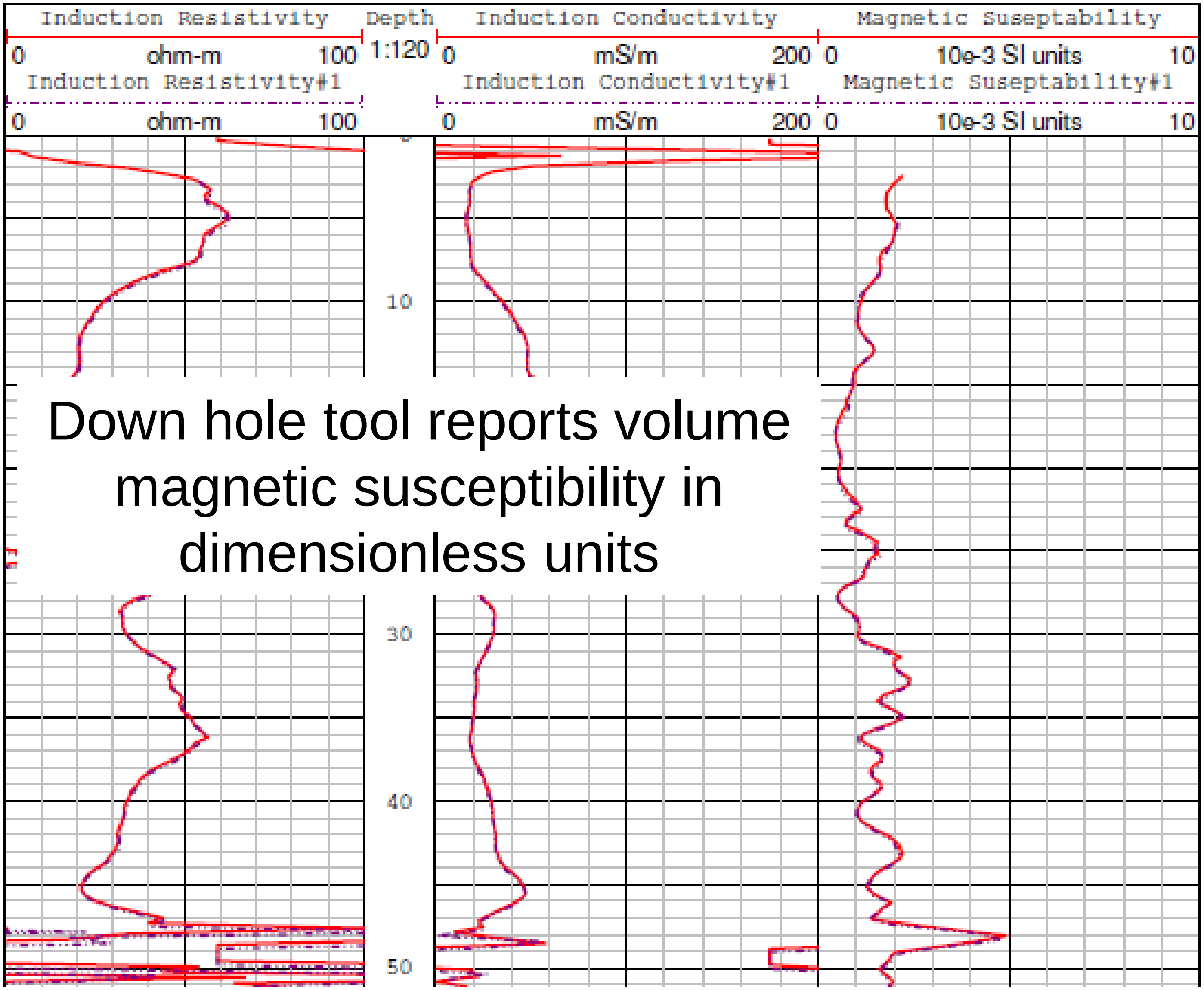

Former Plattsburgh AFB
5/1/1996
DCE First Order Rate Constant (1/year)
10
1
0.1
0.01
1.0E-08
1.0E-07
1.0E-06
1.0E-05
Magnetic Susceptibility (m3 kg-1)
PCE in microcosms
TCE in microcosms
cis-DCE in microcosms
VC in microcosms
DCE at Plattsburgh
VC at Plattsburgh
TCE at Hopewell
cis-DCE Site A at TCAAP
TCE OU-3 at TCAAP



Former Plattsburgh AFB
5/1/1996
DCE First Order Rate Constant (1/year)
10
1
0.1
0.01
1.0E-08
1.0E-07
1.0E-06
1.0E-05
Magnetic Susceptibility (m3 kg-1)
PCE in microcosms
TCE in microcosms
cis-DCE in microcosms
VC in microcosms
DCE at Plattsburgh
VC at Plattsburgh
TCE at Hopewell
cis-DCE Site A at TCAAP
TCE OU-3 at TCAAP

# SECOND CASE STUDY
# ABIOTIC DEGRADATION

Fruit Avenue Plume Superfund Site
A large plume of TCE in a water supply aquifer beneath downtown Albuquerque, NM




Down hole tool reports volume magnetic susceptibility in dimensionless units

# Mass Magnetic Susceptibility

- To calculate Mass Magnetic Susceptibility, the Volume Magnetic Susceptibility is divided by the Bulk Density of the sediment
- At 30% porosity, the Bulk Density is approximately 0.7 * 2,560 kg/m$^3$ or 1,792 kg/m$^3$

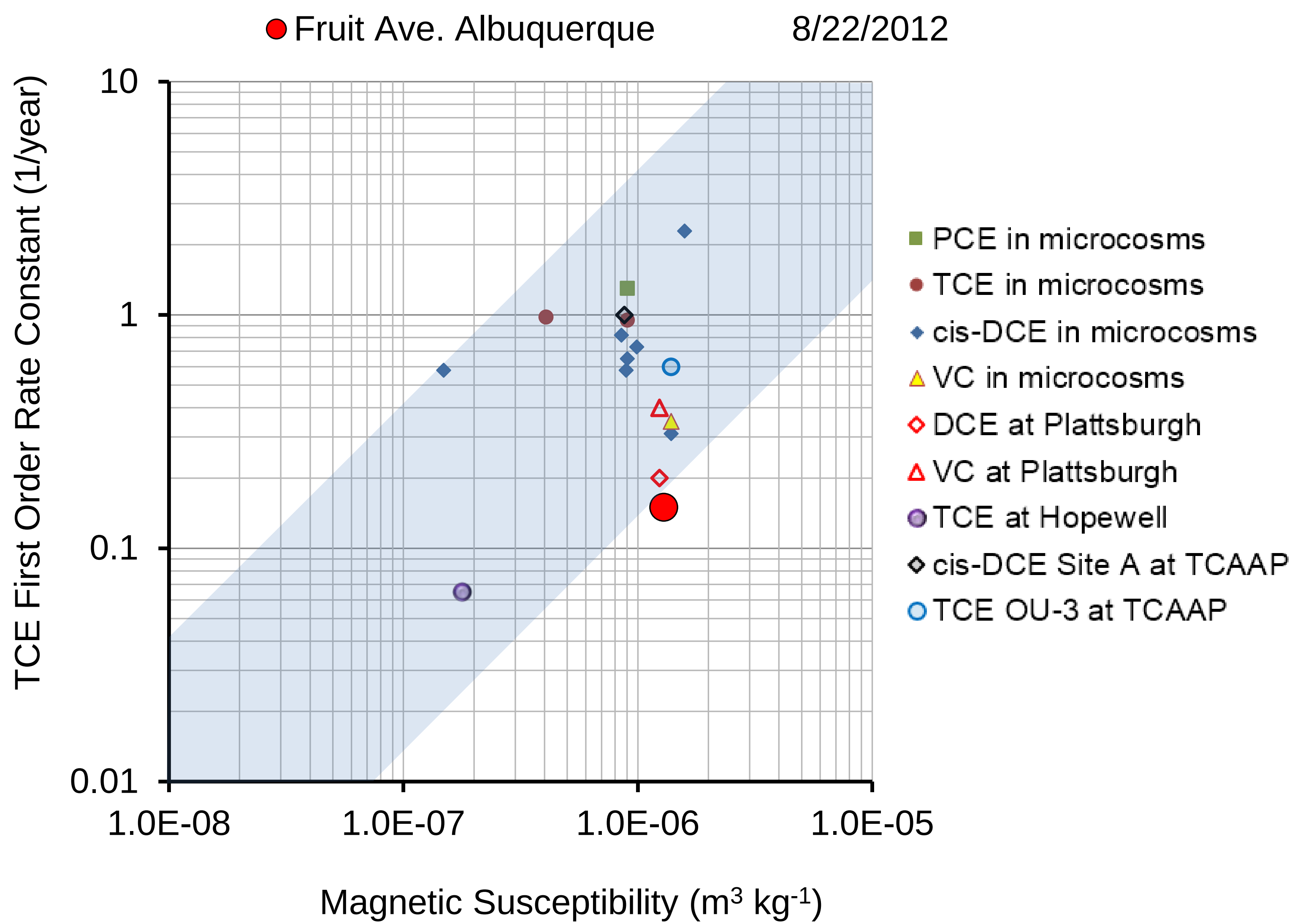
# Magnetic Susceptibility in Sediments Harboring the Fruit Avenue Plume

| Well ID | VMS SI Units x $10^{-3}$ | MMS $m^3/kg$ |
|---|---|---|
| DM-13(D1) | $2.91 \pm 1.85 \times 10^{-3}$ | |
| HSM-12-5 | $1.93 \pm 0.91 \times 10^{-3}$ | |
| MNW-5(D4) | $2.24 \pm 1.40 \times 10^{-3}$ | |
| SFMW-44(D2) | $2.17 \pm 1.11 \times 10^{-3}$ | |
| Average | $2.3 \times 10^{-3}$ | $1.3 \times 10^{-6}$ |

# Point Rate Constants for Attenuation in Wells in the Fruit Avenue Plume

| Well ID | First Order Rate Constant (1/year) |
|---|---|
| Average of 16 wells in source | 0.18 |
| MNW-5-(D1) | 0.10 |
| SFMW-46-(D1/D2) | 0.19 |
| MNW-5-(D2) | 0.14 |
| Grand average | 0.15 |

| | | |
|---|---|---|
| | Overwrite input cells with data specific to your site | The BASELINE is the lower boundary of the blue shape that encompases plausibe rate constants associated with degradation on magnetite |
| | Input | |
| | First order rate constant for degradation per year | Fraction of rate constants in the benchmark data set that exceed the BASELINE to a greater extent than this rate constant |
| PCE | | rate slower than expected |
| TCE | 0.15 | rate slower than expected |
| cis-DCE | | rate slower than expected |
| Vinyl Chloride | | rate slower than expected |
| | Magnetic Suceptibility SI Units ($m^3kg^{-1}$) | |
| | 1.30E-06 | |
| Location and Site | Fruit Ave. Albuquerque | |
| Date | 8/22/2012 | |


Fruit Ave. Albuquerque
8/22/2012
TCE First Order Rate Constant (1/year)
10
1
0.1
0.01
1.0E-08
1.0E-07
1.0E-06
1.0E-05
Magnetic Susceptibility (m3 kg-1)
PCE in microcosms
TCE in microcosms
cis-DCE in microcosms
VC in microcosms
DCE at Plattsburgh
VC at Plattsburgh
TCE at Hopewell
cis-DCE Site A at TCAAP
TCE OU-3 at TCAAP

# Conclusions

- Incorporate new science into a framework consistent with EPA’s OSWER Directive
- Integrate the decision-making framework into an easy to use application called BioPIC
- Guide users in the selection of MNA, biostimulation and bioaugmentation

For additional information, please visit https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201129/ER-201129

Carmen Lebrón, lebron.carmen.a@gmail.com
John T. Wilson, john@scissortailenv.com

# The next webinar is on March 26

***Innovative Tools for Species Inventory, Monitoring, and Management***

http://www.serdp-estcp.org/Tools-and-Training/Webinar-Series/03-26-2015

SERDP DOD • EPA • DOE | ESTCP

# Survey Reminder

*Please take a moment to complete the survey that will pop up on your screen when the webinar ends*